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**ELECTRON TRANSFER PROCESSES ACROSS $\{Mo=S\}$ BOND
IN THIOMOLYBDATES BY EXTERNAL MEDIATORS**

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

by
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to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
JULY, 1988

To those who listen, adapt your speech
Both Virtue and gain are within its reach.

- Thiruvalluvar

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STATEMENT

I hereby declare that the matter embodied in this thesis "Electron Transfer Processes Across {Mo=S} Bond in Thiomolybdates by External Mediators" is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Dr. S. Sarkar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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July 1988

CERTIFICATE

Certified that the work "Electron Transfer Processes Across {Mo=S} Bond in Thiomolybdates by External Mediators" , presented in this thesis has been carried out by Mrs. JAYANTHI CHANDRASEKARAN under my supervision and the same has not been submitted elsewhere for a degree.



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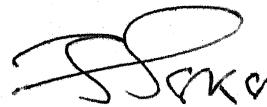
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SYNOPSIS

The thesis entitled, "Electron Transfer Processes Across {Mo=S} Bond in Thiomolybdates by External Mediators" has been divided into five chapters.

Chapter 1 presents an overview of the synthesis and characterization of the various M-S (M = Mo, W) complexes involving electron transfer processes across {M=S} bond. These reactions have been classified as electron transfer in the presence of (i) proton (ii) organic sulfides (iii) polysulfides (iv) sulfur and by (v) thermal influence.

The second chapter outlines the scope of the present work. The possibility of induction of electron transfer by light, heat or external oxidants such as atmospheric oxygen has been discussed. The subtle difference in the reactivity between similar oxo and thio substituted molybdenum compounds has been stressed upon. An approach, exploiting the reactivity of $[\text{MoS}_4]^{2-}$ and $[\text{MoOS}_3]^{2-}$ by the addition of chemical stimuli has been outlined.

Chapter 3 describes the experimental procedures directed towards this research endeavour and has been divided into nine sections. Section 3.1 presents the work-up manipulations of the complexes prepared and the methods used to analyze them. Section 3.2 gives the procedures for the preparation of the starting materials used. An account of the aging process of ammonium

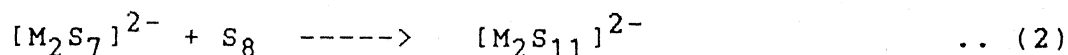
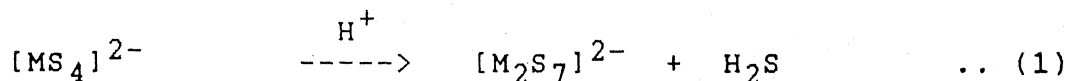
tetrathiomolybdate is given in section 3.3. Freshly prepared $(\text{NH}_4)_2\text{MoS}_4$ has a deep red color but on aging it acquires a mauve-brown tinge which is due to the formation of the pentavalent dinuclear species, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$. Section 3.4 covers the thermal reaction of ammonium tetrathiomolybdate in air, where the final product has been found to be $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$. Section 3.5 deals with the interaction of thiomolybdates and thiotungstates with sulfur in the presence of proton. Acidification of $(\text{XPh}_4)_2[\text{MS}_4]$ and $(\text{XPh}_4)_2[\text{MOS}_3]$ ($\text{X} = \text{P}, \text{As}; \text{M} = \text{Mo}, \text{W}$) in the presence of elemental sulfur in acetonitrile yields compounds of the general formula, $[\text{M}_2(\text{L})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$, ($\text{M} = \text{Mo}, \text{W}; \text{L} = \text{O}, \text{S}$). The molybdenum compounds have also been synthesized without acidification but by using protonated cationic salts of $[\text{MoS}_4]^{2-}$ or $[\text{MoOS}_3]^{2-}$ with elemental sulfur. Section 3.6 describes the reaction of thiomolybdates with sulfur and activated acetylenes. $[\text{MoS}_4]^{2-}$ reacts with S and DBA (dibenzoyl acetylene) to give the tris(dithiolene) complex anion, $[\text{Mo}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]^{2-}$. The anion $[\text{MoOS}_8]^{2-}$ reacts readily with activated acetylene (DBA) to give the dithiolene adduct $[\text{MoO}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^{2-}$. Section 3.7 describes the reactions of thiomolybdates with carbondisulfide. Non-protonated cationic salt of $[\text{MoOS}_3]^{2-}$ reacts with CS_2 under nitrogen at room temperature to yield the tetravalent monomeric complex $[\text{MoO}(\text{CS}_3)(\text{CS}_4)]^{2-}$. When protonated cationic salt (i.e. $(\text{NH}_4)_2\text{MoS}_4$) is used, the dimeric complex having thiocarbonate ligands, $[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_4]^{2-}$ is isolated. When $(\text{Et}_2\text{NH}_2)_2\text{MoS}_4$ is used, CS_2 plays the dual role of inducing electron transfer

across {Mo=S} bond as well as reacting with the cationic part to produce the bidentate dithiocarbamate ($\text{dtc}^- = (\text{S}_2\text{CN}(\text{Et})_2)^-$) ligand. Thus the compound isolated is $[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_2(\text{dtc})_2]$. The reaction of $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$ with CS_2 gives a mononuclear hexavalent complex, $[\text{MoO}(\text{S}_2)(\text{dtc})_2]$ and a dinuclear pentavalent complex, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{dtc})_2]$. Section 3.8 deals with the role of I_2 and $(\text{S}_2\text{O}_8)^{2-}$ as external oxidants towards thiomolybdates. The reaction of $(\text{Et}_2\text{NH}_2)_2\text{MoS}_4$ or $(\text{EtNH}_2)_2\text{MoOS}_3$ with I_2 yields the dinuclear species, $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ or $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ respectively. When $(\text{NH}_4)_2\text{MoS}_4$ is treated with $(\text{S}_2\text{O}_8)^{2-}$ in aqueous medium, $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$, a tetravalent trinuclear cluster along with $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ have been isolated.

The physico-chemical studies to characterize the complexes synthesized have been discussed in the first part of chapter 4. The complexes have been studied by infrared, electronic, electron paramagnetic resonance spectroscopy and cyclic voltammetry.

The second part of chapter 4 focuses on the redistribution of electrons across {Mo=S} bond in thiomolybdates under the influence of external mediators. The formation of the dimer $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ on aging of $(\text{NH}_4)_2\text{MoS}_4$ has been shown to be an example of internal electron transfer reactions induced by atmospheric oxygen followed by hydrolysis. The external oxidant, oxygen, induces intramolecular electron transfer from the sulfido ligands (internal reductant) to the central Mo(VI) atom (internal oxidant).

The formation of the condensed species containing M(VI) of the general formula $[M_2(L)_2(\mu-S)(S_2)_4]^{2-}$, $[M = Mo, W; L = O, S]$ in acidic medium, when $[MS_4]^{2-}$ is treated with sulfur may follow the reaction pathway as summarized below.



$[MoS_4]^{2-}$, either in the presence of proton or sulfur responds to redox condensation reaction. However, under the influence of both proton and sulfur together, as has been done in the present study, the isolation of non reduced condensed bi-metallic species (which is a general reaction applicable to Mo and W systems) has been achieved. The intermediate containing the core $[Mo(VI)-S-Mo(VI)]$ is highly reactive which is stabilized by coordination expansion.

In the reaction of $[MoO(S_4)_2]^{2-}$ with DBA to form the bis-(dithiolene) complex the insertion of acetylene does not take place across the $\{Mo=S\}$ bond; instead it follows a cycloaddition process. The formation of tris(dithiolene) complex on reacting activated acetylene with $[MoS_4]^{2-}$ in the presence of sulfur suggests that the terminal sulfido group can be readily replaced by activated acetylenes.

The formation of the tetravalent complex $[\text{MoO}(\text{CS}_3)(\text{CS}_4)]^{2-}$ by reacting $[\text{MoOS}_3]^{2-}$ with CS_2 in the absence of air is a very rare example of activation of electron transfer across $\{\text{Mo}=\text{S}\}$ bond influenced by a non redox species like CS_2 . Similar induction of electron transfer has been achieved in the reaction of CS_2 with $(\text{NH}_4)_2\text{MoS}_4$, $(\text{Et}_2\text{NH}_2)\text{MoS}_4$ and $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$. But in the latter cases the reaction mixture gives an EPR spectrum characteristic of pentavalent monomeric Mo species whereas in the former case no such intermediate has been observed. The reason for the formation of the Mo(V) monomeric intermediate in the latter reactions has been attributed to the presence of proton present in the cationic part of the thiomolybdates.

The synthesis of $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ from $[\text{MoS}_4]^{2-}$ involves the conversion of four sulfido groups to two persulfido groups and the electrons released are shared equally by the internal oxidant, Mo(VI) and external oxidant I_2 , followed by unavoidable hydrolysis. In the conversion of $[\text{MoS}_4]^{2-}$ to $[\text{Mo}_3\text{S}_{13}]^{2-}$, $(\text{S}_2\text{O}_8)^{2-}$ acts as the external oxidant to generate solely Mo(IV) species. The thesis ends with a few recommendations for future work.

C H A P T E R 1

Molybdenum is unique in that it is the only second row transition metal known to be part of biological processes. The chemistry of molybdenum has been aptly described as among the most complex of the transition elements [1]. The formal oxidation states range from 0 to +6 and the coordination numbers span from 4 to 8. Mononuclear, dinuclear and polynuclear compounds are known virtually in all oxidation states [2]. When we consider the role of molybdenum in life processes, it is the combination of molybdenum with donor groups i.e. ligands which generates the biological activity. In all the molybdenum enzymes so far reported, sulfur is an integral part of the prosthetic groups. The enzymes which are presently considered to involve molybdenum as an essential constituent, are listed in Table 1.1. [3, 4].

The compounds containing exclusively molybdenum and sulfur are known since 19th century. The oxo ligands of the molybdate, $[\text{MoO}_4]^{2-}$, can be replaced successively by sulfido groups by the action of H_2S on aqueous alkaline solutions of molybdates [5, 6]. The whole series of individual compounds $[\text{MO}_{4-n}\text{S}_n]^{2-}$ ($n = 1 - 4$) have been isolated as $(\text{NH}_4)^+$ salts except $[\text{MO}_3\text{S}]^{2-}$ which is known to exist only in solution [7, 8]. These thio derivatives have achieved great deal of attention, thanks to the pioneering investigations of Müller and coworkers [9, 10]. As will be seen in the following sections, the thiometallates have become the starting

Table 1.1 Molybdenum Enzymes [3, 4]

Enzyme	Mo ^a Content	Other Cofactors	Substrate	Source
Xanthine Oxidase	2	4Fe ₂ S ₂ , 4FAD	purines	bovine milk
Xanthine dehydrogenase	2	4Fe ₂ S ₂ , 4FAD	purines	animals, micro-organisms
Aldehyde Oxidase	2	4Fe ₂ S ₂ , 4FAD	aldehydes	animals
Sulfite Oxidase	2	2 heme	(SO ₃) ²⁻	animals, micro-organisms
Nitrate Reductase	4 ^b	4 heme, 4FAD ^b	(NO ₃) ⁻	micro-organisms
Nitrate Reductase	1 ^b	4 Fe ₄ S ₄ ^b	(NO ₃) ⁻	micro-organisms
Formate Dehydrogenases	2 - 4	heme, Fe _n S _n , W, Se	CO ₂ , (HCOO) ⁻	micro-organisms
Pyridoxal Oxidase	(2) ^{b,c}	(4Fe ₂ S ₂ , 4FAD) ^{b,c}	pyridoxal	insects
Mo Protein	1	6Fe ₂ S ₂ ^b	?	Desulfo-vibrio gigas
Nitrogenase	2	24 - 32 Fe (Fe/S centers)	N ₂	Clostridium Pasteurianum

^aAtoms/molecule; ^bFor specific organism; ^ctentative

material for the synthesis of a number of molybdenum-sulfur compounds. The substitution of sulfur for molybdenum, although does not alter the structure in any unusual way, the oxidation of two sulfido groups to form a disulfido ligand (which occurs much more readily than the oxidation of two oxo groups to a peroxo entity) introduces an extra dimension in the reactivity. Exploitation in this direction have led to a rich coordination chemistry of molybdenum-sulfur complexes and much of this work has been reviewed [9, 10].

Interestingly even in the nineteenth century, compounds having -S-S- linkages have been proposed perhaps based simply on the elemental analysis and reactivity of the compound. The lack of sophisticated physico-chemical techniques have not deterred Hofmann [11] from proposing a perthiomolybdic acid, H_2MoS_5 (corresponding to permolybdic acid) with a disulfido group. With the advent of X-ray crystallography and spectrochemical methods of analysis in the later half of the this century, the structure has been made available, which could be best described as $[\text{Mo}_2\text{S}_{10}]^{2-}$ [12]. A persulfide $[\text{MoS}_4]$ has been reported to form when $[\text{MoO}_4]^{2-}$ is treated with H_2S in excess [13]. This complex could well be the recently reported $[\text{Mo}_2\text{S}_8]^{2-}$ by Stiefel and coworkers [14]. Here one has to bear in mind that while proposing a structure based on elemental analysis and reactivity alone, it is quite possible to arrive at a different number for hydrogen. Even today analyzing hydrogen at a low concentration poses a lot of problem.

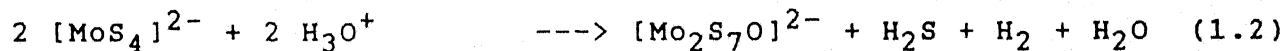
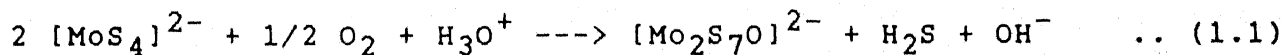
The amorphous dark brown molybdenum trisulfide has been formulated as MoS_3 having Mo in its highest oxidation state, +6. But the recent EXAFS studies [15], XPS data [16] and the S-S stretching vibration in the infrared spectrum [17] have led to the possibility of MoS_3 having a chain structure with repeating $\{\text{Mo}_2(\text{V})(\text{S}^{2-})_4(\text{S}_2^{2-})\}$ units [16]. Now, looking at the synthesis of this compound, there are two methods reported in the literature [18, 19]. One is the thermal decomposition of hexavalent $(\text{NH}_4)_2[\text{MoS}_4]$ [18] and the other is the acidification of a solution of $[\text{MoS}_4]^{2-}$ [19]. The reduction of molybdenum center or in other words, electron flow across the molybdenum-sulfur bond has been achieved either under thermal conditions or by the use of proton. The persulfide formation mentioned earlier [13] can be viewed as a result of the action of polysulfide on $[\text{MoO}_4]^{2-}$, as excess of H_2S is used in the reaction. The polysulfide can be treated as an oxidizing agent. Then under the influence of polysulfide acting as an external oxidant electron transfer across $\{\text{Mo-S}\}$ bond is facilitated. The electron transfer is also feasible with the aid of photon. The photochemical induction using visible light has resulted in the conversion of Mo(V) sulfido complex, $[(\text{Cp})_2\text{Mo}_2\text{S}_4]$ to a Mo(IV) disulfido complex $[(\text{Cp})_2\text{Mo}_2\text{S}_2(\text{S}_2)]$ [20]. Thus the presence of an inducing agent in the form of external oxidant, phonon or proton can bring about electron transfer reactions. Tungsten, the heavier congener of molybdenum differs in that the former is much more resistant to reduction. But the recent exploitations of induced electron

transfer processes have made it possible to synthesize a number of W-S compounds in lower oxidation states [21-23]. In the following sections a brief overview of the synthesis of various M-S (M = Mo, W) complexes using any of the above strategies has been presented.

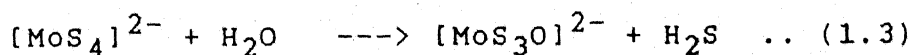
Electron transfer in the presence of proton

As seen in the preceding section, the amorphous MoS_3 has been isolated from an acidified solution of $[\text{MoS}_4]^{2-}$ [19]. The tungsten analog WS_3 , again amorphous in nature, may also be prepared by acid treatment of $[\text{WS}_4]^{2-}$ [19]. A working model for the structure of WS_3 has been proposed based on EXAFS studies [15].

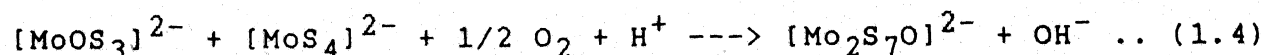
Controlled acidification of $(\text{NH}_4)_2\text{MoS}_4$ followed by addition of $[\text{nBu}_4\text{N}]\text{Cl}$ has resulted in the formation of the unsymmetrical oxo-sulfido complex $(\text{nBu}_4\text{N})_2[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]$ [24]. The formation of this complex has been viewed as the result of any of the two plausible redox-condensation reactions given in eqs. 1.1 and 1.2 [24].



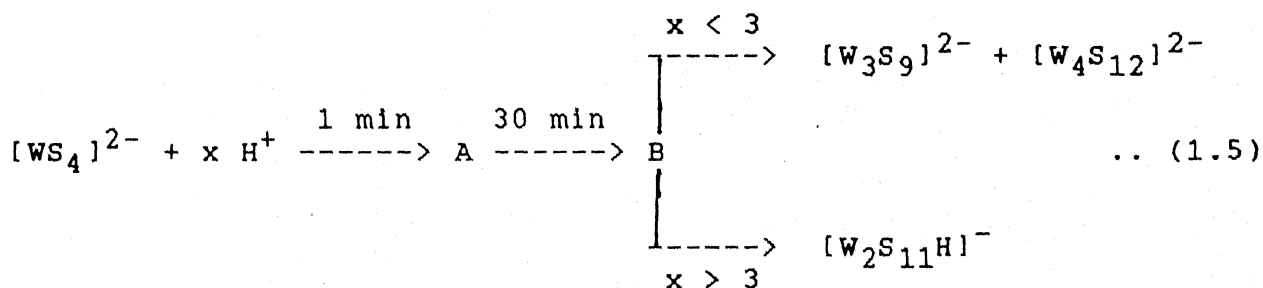
The first step of the redox condensation in eq. 1.1 has been proposed as



followed by reaction of the intermediate,

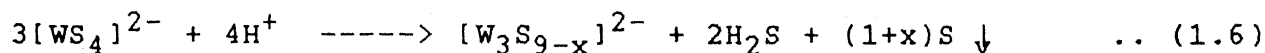


A recent report reveals the formation of $(\text{PPh}_4)_2\text{Mo}_3\text{S}_9$, when $(\text{PPh}_4)_2\text{MoS}_4$ is acidified with glacial acetic acid followed by addition of $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ [25]. The role of manganous ion is not clear. But when $(\text{PPh}_4)_2\text{WS}_4$ is used, condensation takes place leading to the formation of $(\text{PPh}_4)_2[\text{W}_2\text{S}_{11}]$ [25]. The presence of LiCl in the above reaction leads to $[\text{W}_3\text{S}_9]^{2-}$ and CrCl_3 yields only $[\text{W}_4\text{S}_{12}]^{2-}$. In fact, manganous chloride has been used in an attempt to prepare the $[\text{Mn}(\text{WS}_4)_2]^{2-}$ dianion [25], but the isolated product has been characterized as $(\text{PPh}_4)_2\text{W}_2\text{S}_{11}$ with no incorporation of Mn. $(\text{PPh}_4)_2\text{WS}_4$ when refluxed with sulfur followed by acidification gives rise to the protonated complex $[\text{W}_2\text{S}_{11}\text{H}]^-$ [26]. It has been proposed that the formation of $[\text{W}_3\text{S}_9]^{2-}$ [27], $[\text{W}_4\text{S}_{12}]^{2-}$ [28] and $[\text{W}_2\text{S}_{11}\text{H}]^-$ from $[\text{WS}_4]^{2-}$ proceeds via two intermediates according to equation 1.5 [26].



The low yield of the $[\text{W}_2\text{S}_{11}\text{H}]^-$ has been attributed to the different sulfur coordination modes borne by tungsten. It has been proposed that the disulfide ligands $(\text{S}_2)^{2-}$ in $[\text{W}_2\text{S}_{11}\text{H}]^-$ have been formed in situ by the oxidation of S^{2-} groups of $[\text{WS}_4]^{2-}$ on acidification without external addition of $(\text{S}_2)^{2-}$ dianions.

The preparation of $(PPN)_2[W_3S_8]$ ($PPN = \text{bis}(\text{triphenylphosphoranylidene}) \text{ ammonium}$), is achieved by the reaction of $(NH_4)_2[WS_4]$ with H_2SO_4 , followed by addition of $(PPN)Cl$ in methanolic solution [29]. The stoichiometry has been described as,



$x = 0 \text{ or } 1$

The reactions of $[WS_4]^{2-}$ with acids are also known to lead to a mixture of thiotungstate anions $[W_3OS_8]^{2-}$, $[W_4S_{12}]^{2-}$ and $[WS_3(SH)]^-$ [27, 28] which have been separated and characterized individually. The reduction of an acidified solution of tetrathiotungstate with $NaBH_4$ results in the formation of the incomplete cubane type $[W_3S_4]^{4+}$ aqua ion [30].

Electron transfer in the presence of organic sulfides

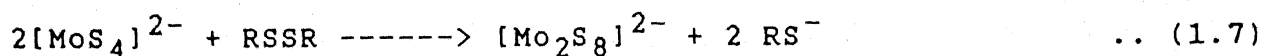
When $(PPh_4)_2MoS_4$ is reacted with dibenzyl trisulfide, the resulting compound has a formulation $(PPh_4)_2Mo_2S_{10/12} \cdot 1/2DMF$ [31]. The site of $[Mo_2S_{10}]^{2-}$ anion is partially occupied by $[Mo_2S_{12}]^{2-}$ anion and the formation of this compound has been attributed to be part of a very complex system of equilibria [31]. The mechanism could well be that the organic trisulfide acts as an external oxidant which facilitates the oxidation of S^{2-} ligands to $(S_2)^{2-}$ and the resulting electrons are used up in the reduction of molybdenum center.

The reaction of $[MoS_4]^{2-}$ with tetramethylthiuramdisulfide, (TMDs) leads to the isolation of a mononuclear $Mo(V)$ complex, $[Mo(S_2)(S_2CNET_2)_3]$ [32]. In this case the Mo center has been

reduced by internal electron transfer from the bound sulfide ligands, while the latter are concomitantly oxidized to bound $(S_2)^{2-}$ [32]. Thus this method has proven possible to produce new reduced Mo-S complexes by adding oxidants to $[MoS_4]^{2-}$ which contains Mo in its highest oxidation state. When $(NH_4)_2MoO_2S_2$ is reacted with TMDS, a hexavalent blue compound $[MoO(S_2)(S_2CNR_2)_2]$ is isolated for which a ligand based electron transfer reaction has been proposed [23, 32]. Here the substitution of sulfido by oxo ligands seems to hinder the reduction, thus enabling a ligand ---> ligand electron flow rather than ligand ---> metal electron flow.

$[MoS(S_2)(S_2CNR_2)_2]$ has not been isolated till date. But the tungsten counter part $[WS(S_2)(S_2CNR_2)_2]$ has been isolated by the reaction of TMDS on $[WS_4]^{2-}$ at room temperature under argon [32]. Here again a ligand based redox reaction has been suggested to be operative.

One equivalent of $C_6H_5-S-S-C_6H_5$ has been found to react with 2 equivalents of $(NH_4)_2MoS_4$ in DMF at $90^\circ C$ to yield a pentavalent binary molybdenum sulfide $[Mo_2S_2(\mu-S)_2(S_2)_2]^{2-}$ [14]. The stoichiometry has been given as shown below.



The conversion of four S^{2-} ligands to two $(S_2)^{2-}$ ligands results in the release of four electrons. The external oxidant RSSR takes up two electrons and each of the two Mo atoms takes up one

electron. The ease with which internal electron transfer occurs has been attributed to the ability of sulfide/polysulfide ligand systems to exhibit energy levels both above and below the 4d levels of molybdenum [14].

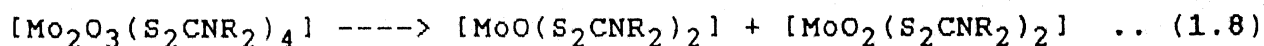
The dichromate analog of thiomolybdate $[\text{Mo}_2\text{S}_7]^{2-}$ has been isolated by Coucouvanis and coworkers [33] with the aid of dibenzyl trisulfide. They have reacted $(\text{PPh}_4)_2[\text{Mo}_2\text{S}_6]$ [33] with the trisulfide to isolate $(\text{PPh}_4)_2[\text{Mo}_2\text{S}_7]$ in good yields. One of the pentavalent molybdenum centers has been oxidized in this reaction, with the conversion of a sulfido group to disulfido group under the influence of trisulfide.

Polysulfide induced electron transfer process

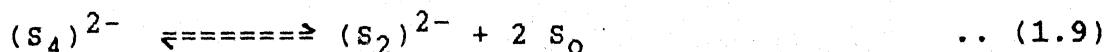
When ammonium heptamolybdate is treated with polysulfide solution, reduction of molybdenum center takes place with the formation of the sulfur rich molybdenum compound $[\text{Mo}_2\text{S}_{12}]^{2-}$ [34]. This compound consists of exclusively $(\text{S}_2)^{2-}$ ligands. The formation of tetrathiomolybdate *in situ* and then reduction of the metal center and condensation has been invoked to explain the formation of the final product, $[\text{Mo}_2\text{S}_{12}]^{2-}$. The use of excess polysulfide, an oxidizing agent, suggests that the reaction could be induced electron transfer type where polysulfide functions as an external oxidant. The same compound can be synthesized by keeping a solution of $(\text{NH}_4)_2\text{MoS}_4$ in water saturated with H_2S for a very long time. $\text{H}_2\text{S}/\text{H}_2\text{O}$ system can generate elemental sulfur specially in the presence of metal ions [35]. Sulfur with H_2S

might generate polysulfide and the concentration of polysulfide dictates the formation of the said compound. It has been observed that a fairly concentrated solution of polysulfide is essential to get the compound in good yield. When the temperature is raised to 90°C in the above reaction, further reduction of molybdenum center takes place to yield the cluster $[\text{Mo}_3\text{S}_{13}]^{2-}$ [36-39]. This compound contains sulfur atoms in three different states of bonding. Both, the concentration of polysulfide and temperature are the crucial factors for the formation of the trinuclear species $[\text{Mo}_3\text{S}_{13}]^{2-}$ [38, 39].

Na_2S_4 [40], when reacted with the pentavalent dimeric oxo complex $[\text{Mo}_2\text{O}_3(\text{S}_2\text{CNR}_2)_4]$, the well known hexavalent monomeric compound $[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$ is formed [41]. A disulfur radical attack (from the dissociation of Na_2S_4 on the {Mo-O} bridge is proposed for the cleavage of the {Mo-O} bridge. The mechanism might as well be that pentavalent compound disproportionates as follows:



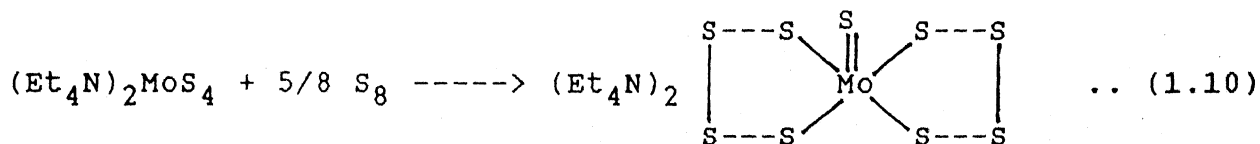
The sulfur which is in equilibrium with the polysulfide, $(\text{S}_4)^{2-}$ (as shown below)



may oxidize the tetravalent complex to the reported hexavalent compound $[\text{Mo}^{\text{VI}}\text{O}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$. In fact, this mechanism gets more credence with the report that $[\text{Mo}^{\text{IV}}\text{O}(\text{S}_2\text{CNR}_2)_2]$ has been oxidized by elemental sulfur to yield $[\text{Mo}^{\text{VI}}\text{O}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$ [42].

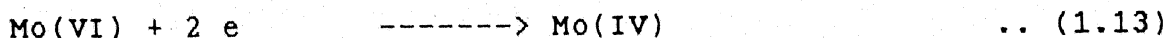
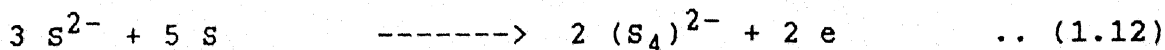
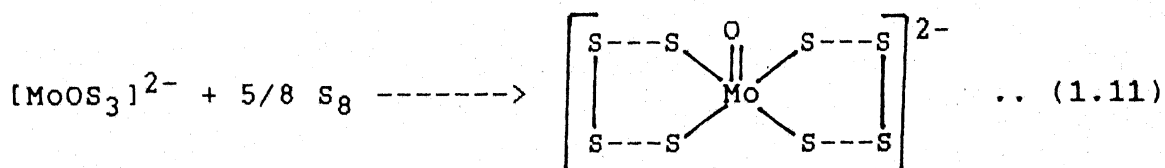
Sulfur induced electron transfer processes

The $[\text{MoS}_4]^{2-}$ anions react with elemental sulfur (or 'active' sulfur reagents such as organic trisulfides) to afford the novel sulfur ring complex $[\text{MoS}_9]^{2-}$ [31, 43, 44] as shown in eq. 1.10.

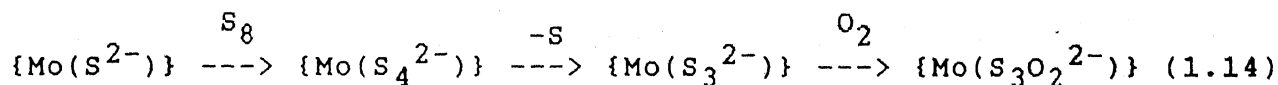


It has been viewed that the oxidation of coordinated S^{2-} to $(\text{S}_4)^{2-}$ and the coupled reduction of Mo(VI) to Mo(IV) are brought about by an induced electron transfer pathway wherein the electron transfer occurs from the coordinated S^{2-} to the molybdenum center.

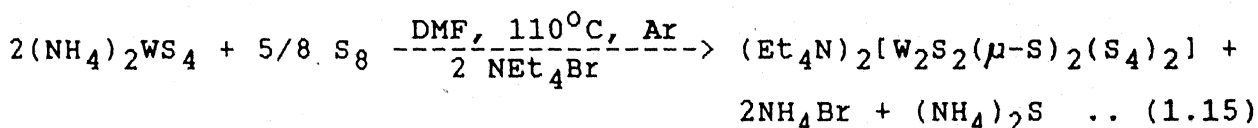
The oxo analog $(\text{Et}_4\text{N})_2[\text{MoOS}_8]$ has been prepared in more than one way [31, 45]. The hydrolysis of $[\text{MoS}_9]^{2-}$ yields the oxo product $[\text{MoOS}_8]^{2-}$ [31]. The reaction of $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$ with elemental sulfur in presence of Et_4NBr also yields $(\text{Et}_4\text{N})_2[\text{MoOS}_8]$ in good yields [45]. Here too, the mechanism invokes sulfur as an external oxidant. The electron balanced reactions are shown below.



When $(PPh_4)_2MoOS_3$ is reacted with sulfur in DMF under aerobic conditions, a compound containing dithiosulfate ligand, $[(S_2)(O)Mo(\mu-S)_2Mo(O)(S_3O_2)]^{2-}$ has been isolated [46]. The formation of the dithiosulfate ligand has been viewed via $(S_3)^{2-}$ which gets oxidized to $(S_3O_2)^{2-}$ as shown in equation 1.14.

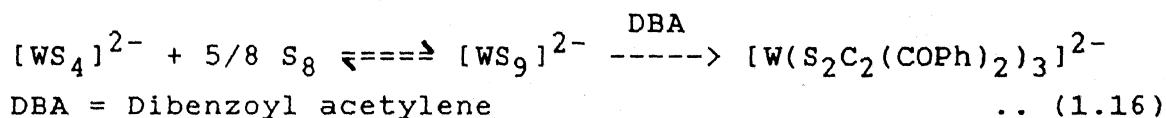


Sulfur reacts with $(NH_4)_2MoS_4$ at $95^\circ C$ under argon atmosphere in DMF, to yield the black crystalline dimer $[Mo_2S_2(\mu-S)_2(S_4)_2]^{2-}$ [47]. The tungsten analog, $[W_2S_2(\mu-S)_2(S_4)_2]^{2-}$ has been prepared from $(NH_4)_2WS_4$ and sulfur at $110^\circ C$ [47]. This reaction has been observed to proceed only under a strong jet of argon gas on the surface of the reaction mixture. If the purging of argon is not maintained W(VI) species are also obtained along with the product.



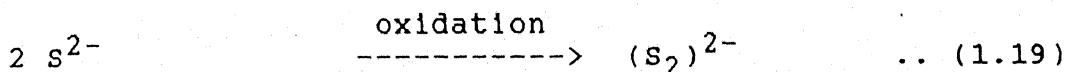
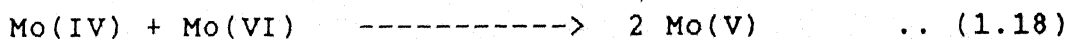
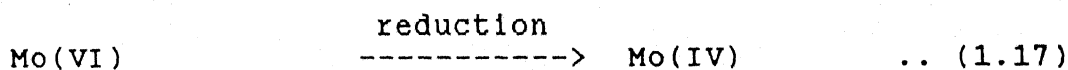
In this case, $(NH_4)_2S$, one of the by products (eq. 1.15) might combine with elemental sulfur to form ammonium polysulfide which in turn might react with $[W_2S_2(\mu-S)_2(S_4)_2]^{2-}$ in a complimentary fashion pushing the equilibrium backwards, thereby forming $[WS_4]^{2-}$. Thus the role of argon jet is to remove the by product $(NH_4)_2S$ and to push the reaction in the forward direction [22].

The formation of $[\text{W}(\text{dithiolene})_3]^{2-}$ has been observed when $[\text{WS}_4]^{2-}$ is reacted with sulfur in the presence of activated acetylenes [48]. The molybdenum analog $[\text{Mo}(\text{dithiolene})_3]^{2-}$ is obtained by using $[\text{MoS}_9]^{2-}$ as starting material [49, 50]. Thus a clue to the reaction pathway can be taken from the molybdenum systems that $[\text{WS}_9]^{2-}$ may be formed in situ. Even though the isolation of this elusive species has not been achieved so far, it is possible that $[\text{WS}_9]^{2-}$ is formed via an induced electron transfer process (as has been seen in the formation of $[\text{MoS}_9]^{2-}$), shown in equation 1.16.



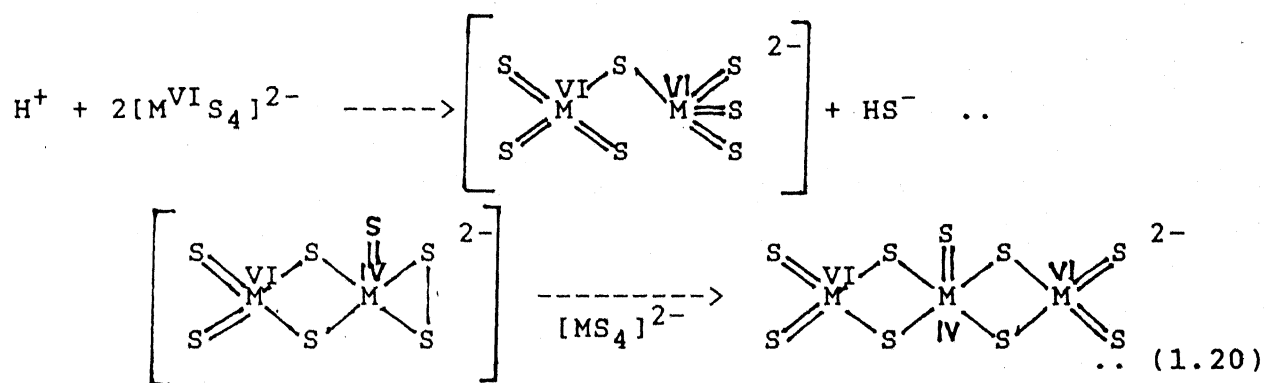
Thermally induced electron transfer process

When an aqueous solution of $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ saturated with H_2S , is heated reduction takes place at the molybdenum center to form the pentavalent dimeric compound $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ [51, 52]. The compound has been isolated as the tetramethylammonium salt. The following mechanism has been proposed [52].



A recent proposal on the mechanism of this reaction invokes induced electron transfer process where oxygen plays the role of external oxidant [22].

Heating $(\text{NH}_4)_2\text{MS}_4$ ($\text{M} = \text{Mo}, \text{W}$) in DMF under argon leads to the formation of the trinuclear complex anion $[\text{M}_3\text{S}_9]^{2-}$ [53]. The structure of this complex shows two external tetrahedral $\{\text{MS}_4\}$ units chelating a central square pyramidal $\{\text{Mo(IV)-S}\}$ unit. The need of a proton in the form of protonated cationic salts like $(\text{NH}_4)^+$ or $(\text{NEt}_3\text{H})^+$ has been found to be necessary for the formation of this binary cluster complex, which is illustrated in equation 1.20.

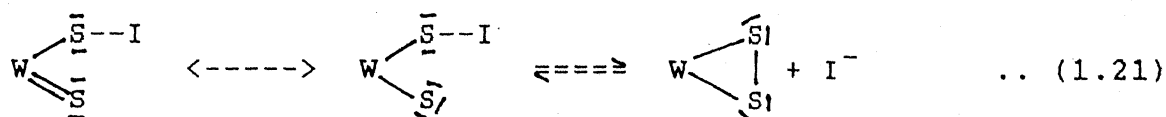


In the case of tungsten elevated temperature is found to be necessary for the formation of $[\text{W}_3\text{S}_9]^{2-}$. The presence of air and moisture leads to the formation of $[\text{W}_3\text{OS}_8]^{2-}$ where terminal sulfur, $[\text{W}_3\text{S}_9]^{2-}$ is replaced by oxygen [53]. It is interesting to note that $[\text{Mo}_3\text{S}_9]^{2-}$ is not easily hydrolyzed to $[\text{Mo}_3\text{OS}_8]^{2-}$.

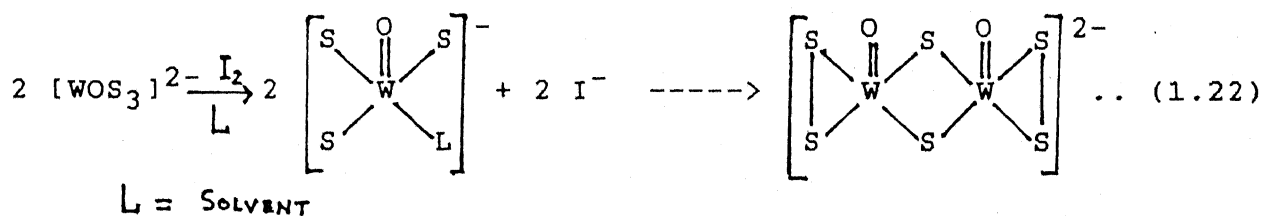
Reaction of $[\text{Mo}(\text{CO})_6]$ with $[\text{Hg}(\text{S}_2\text{CNet}_2)_2]$ under nitrogen in refluxing toluene goes through a series of reactions leading to the isolation of $[\text{Mo}^{\text{V}}\text{O}(\text{S}_2\text{CNet}_2)_3]$ [54]. The possibility of this compound existing as a monomer in solution and dimer in solid state has not been ruled out. The source of oxygen in the final product has not been discussed in this reaction. It is quite possible that the source of oxygen may be an artefact.

Other reactions

The reaction of $[\text{WOS}_3]^{2-}$ with I_2 , $\text{S}_2\text{O}_4^{2-}$, peroxide or disulfide leads to the formation $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ [21, 22]. The process can be viewed as shown in equation 1.21.



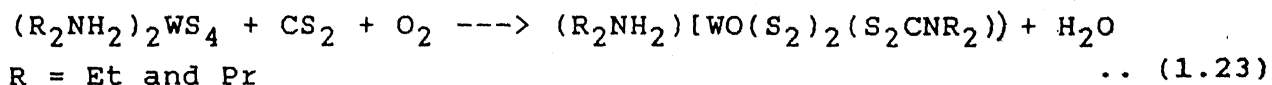
The intermediate W(V) species have been assumed to dimerize to give the final product as shown in equation 1.22.



Interestingly, $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ on treatment with methanolic polysulfide solution yields the starting material, $[\text{WOS}_3]^{2-}$, where polysulfide has been found to function as an external reductant. The latter reaction is very similar to the reaction of $[\text{MoS}_9]^{2-}$ with dithiol to yield $[\text{MoS}_4]^{2-}$, where dithiol functions as an external reductant [55].

The reaction between $(\text{R}_2\text{NH}_2)_2\text{WOS}_3$ and CS_2 in the presence of oxygen yields $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2]$ [56]. Though the reactant and the product maintain hexavalent state, the participation of W has been revealed by way of EPR signal characteristic of W(V). Thus it has been established that oxygen acts as an external oxidant to induce the electron transfer across W-S bond [56].

$(R_2NH_2)_2WS_4$ reacts with CS_2 in presence of oxygen leading to the formation of $(R_2NH_2)[WO(S_2)_2(S_2CNR_2)]$ [57, 58]. This reaction has also been found to be analogous to the earlier one, where EPR signal characteristic of $W(V)$ and O_2^- suggests a very similar induced electron transfer reaction concealed under purely ligand based reaction.



PHYSICAL MEASUREMENTS

Vibrational Spectra :

The infrared spectra of the thiomolybdate and thiotungstate species have been examined in detail [59 - 62]. The free thio-metallates have characteristic $\{M-S\}$ and $\{M-O\}$ ($M = Mo, W$) stretching vibrations ($\nu(M-S)$, $400 - 500\text{ cm}^{-1}$; $\nu(M-O)$, $800 - 1000\text{ cm}^{-1}$) in their infrared and Raman spectra. For thiomolybdates and thiotungstates, as the oxidation state of the central metal increases, the $\nu(M-O_t)$ and $\nu(M-S_t)$, ($t = \text{terminal}$) absorbs at a lower wavenumber (i.e. higher wavelength). Disulfur complexes can be broadly classified into three types as shown below [63].

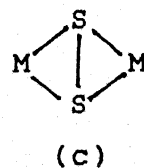
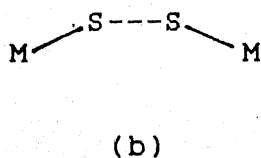


Table 1.2 Infrared Spectral Data of [M(VI)-S] Complexes in cm^{-1}

Compound	$\nu(\text{M=O})$	$\nu(\text{M=S})$	$\nu(\text{S-S})$	Ref
$(\text{NH}_4)_2\text{MoS}_4$	---	476	---	9
$(\text{NH}_4)_2\text{WS}_4$	---	458	---	9
Cs_2MoOS_3	854	473	---	9
Cs_2WOS_3	872	457	---	9
$(\text{NH}_4)_2\text{MoO}_2\text{S}_2$	830, 792	490	---	77
$(\text{NH}_4)_2\text{WO}_2\text{S}_2$	850, 795	470	---	77
$[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNet}_2)_2]$	908, 922	---	560	82
$[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNPr}_2)_2]$	916	---	555	41
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CNet}_2)_2]$	---	500	550	32
$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNet}_2)_2]$	940	---	552	56
$(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNet}_2)]$	880	---	540	58

M = Mo, W.

Table 1.3 Infrared Spectral Data of [M(V)-S] (M = Mo, W) Complexes in cm

Compound	$\nu(\text{M=O})$	$\nu(\text{M=S})$	$\nu(\text{S-S})$	$\nu(\text{M-S}_{\text{br}})$	$\nu(\text{M-S}_n)$	Ref
$(\text{PPh}_4)_2\text{Mo}_2\text{S}_6$	---	503	---	475, 452	---	33
$(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6]$	---	---	550, 551	---	382, 361 354	34
$(\text{PPh}_4)_2\text{Mo}_2\text{S}_7$	---	504	---	480, 454	---	33
$(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]$	925	---	516, 508	467	357, 321	51
$(\text{Me}_4\text{N})_2[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]$	950, 940	---	520	450	335	21
$(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]$	940	N.R	518	460	350	24
$(\text{Et}_4\text{N})_2[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]$	---	535	520	460	350	14
$(\text{Et}_4\text{N})_2[\text{W}_2\text{S}_2(\mu\text{-S})_2(\text{S}_4)_2]$	---	---	555	---	---	47
$[\text{Mo}(\text{S}_2)(\text{S}_2\text{CNEt}_2)_3]$	995	---	---	---	---	32
$[\text{MoO}(\text{S}_2\text{CNEt}_2)_3]$	---	506, 495	---	---	---	54

br = bridging ; n = terminal ; N.R = Not reported.

Table 1.4 Infrared Spectral Data of [M(IV)-S] Complexes in cm^{-1}

Compound	$\nu(\text{Mo}=\text{O})$	$\nu(\text{Mo}=\text{S})$	$\nu(\text{S}-\text{S})$	$\nu(\text{M}-\text{S}_{\text{br}})$	Ref
$[\text{MoS}(\text{S}_4)_2]^{2-}$	---	525	---	---	31
$[\text{MoO}(\text{S}_4)_2]^{2-}$	930	---	---	---	31
$[\text{Mo}_3\text{S}_{13}]^{2-}$	---	---	544	---	36
$[\text{MoS}(\text{MoS}_4)_2]^{2-}$	---	527	---	---	53
$[\text{WS}(\text{WS}_4)_2]^{2-}$	---	525, 490 485	---	465, 435	53
$[\text{WO}(\text{WS}_4)_2]^{2-}$	970	495	---	465, 453	53

M = Mo, W.

In all these complexes, the $\nu(\text{S-S})$ frequencies range from ca. $480\text{--}600\text{ cm}^{-1}$. The charge distribution in disulfur complexes is somewhere between that for $(\text{S}_2)^-$ and for $(\text{S}_2)^{2-}$ [63]. But the coupling of the $\nu(\text{S-S})$ vibration with the $\nu(\text{M-S})$ vibrations may lead to higher $\nu(\text{S-S})$ values which have been observed by isotopic substitution of ^{92}Mo by ^{100}Mo in $[\text{Mo}_2(\text{S}_2)_6]^{2-}$ and $[\text{Mo}_3\text{S}(\text{S}_2)_6]^{2-}$ [64]. The IR spectral data of some of the typical examples are listed in Tables 1.2 - 1.4.

Electronic Spectroscopy :

The free ligands, $[\text{MoS}_4]^{2-}$ is colored red and $[\text{WS}_4]^{2-}$ is yellow-orange due to the tailing of the intense sulfur to metal charge transfer bands into the visible region of the spectrum [65]. Mo and W are in their highest oxidation states and therefore no d-d transition occurs. In the disulfur complexes of the type $\text{M} \begin{smallmatrix} \text{S} \\ | \\ \text{S}^* \end{smallmatrix}$, the π^* orbital of $(\text{S}_2)^{2-}$ splits into a strongly interacting π_h^* orbital in the MS_2 plane and a weakly interacting π_v orbital perpendicular to the MS_2 plane [66]. The optical spectrum of $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ shows transitions at 2.7 and 3.35 eV and the corresponding transitions for $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ shows transitions at 2.16 and 2.65 eV. The first transition has been assigned to a charge-transfer excitation from the $(\text{S}_2)^{2-}$ diatomics to the $\{\text{Mo-O}\}$ and $\{\text{Mo-S}_t\}$ antibonding orbitals respectively [67]. The second transition has been attributed to a charge-transfer excitation from the bridging sulfur atoms to the same acceptor levels. Due to the strong stabilization of S_t bonding levels by σ and π bonding with Mo, both the $(\text{S}_2)^{2-}$ to Mo and bridging S to

Table 1.5 Electronic Absorption Bands of M-S (M = Mo, W)
Complexes

Compound	Color	Band maxima λ (nm)	Ref
$[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	Blue	581, 394	82
$[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	Brown	485, 438 340, 320	56
$[\text{WS}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$	Green	602, 394, 360	32
$(\text{Et}_2\text{NH}_2)[\text{WO}(\text{S}_2)_2(\text{S}_2\text{CNET}_2)]$	Red-brown	480, 412, 322	58
$[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$	Red-orange	463, 370, 305, 278	51
$[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$	Dark Red	475, 390, 305 273, 233	24
$[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$	Purple	573, 467, 295	14
$[\text{W}_2\text{S}_2(\mu\text{-S})_2(\text{WS}_4)_2]^{2-}$	Dark red	385, 294	28
$[\text{Mo}_2(\text{S}_2)_6]^{2-}$	Black-green	769, 625, 500 417, 357, 313	34
$[\text{Mo}_2\text{S}_6]^{2-}$	Dark red	482, 454, 362 310, 290	33
$[\text{Mo}_2\text{S}_7]^{2-}$	Brown-red	560, 452, 422 362, 295	33
$[\text{Mo}_3(\text{S})(\text{S}_2)_6]^{2-}$	Red	541, 465 370, 333	38
$[\text{MoO}(\text{S}_4)_2]^{2-}$	Green	555, 475, 316	31
$[\text{MoS}(\text{S}_4)_2]^{2-}$	Red	470, 405 340, 316	31
$[\text{Mo}(\text{S})(\text{MoS}_4)_2]^{2-}$	Dark red	460, 270	53
$[\text{WS}(\text{WS}_4)_2]^{2-}$	Golden yellow	392, 271	53
$[\text{WO}(\text{WS}_4)_2]^{2-}$	Red-orange	442, 378	53

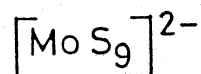
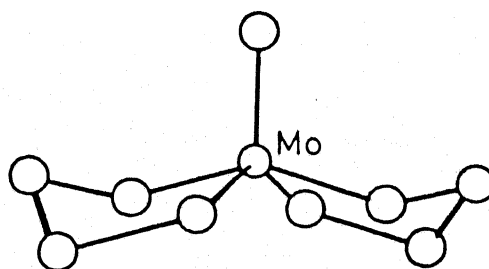
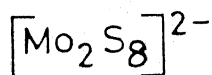
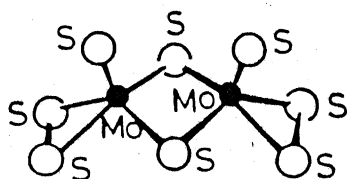
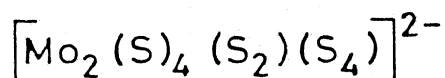
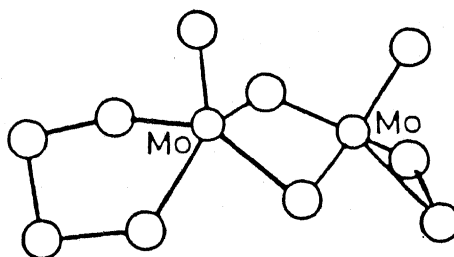
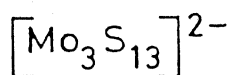
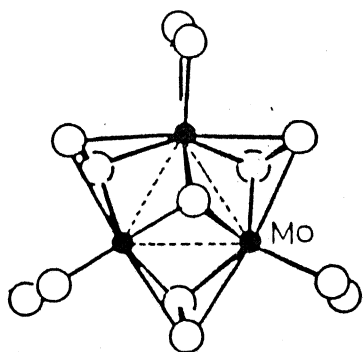
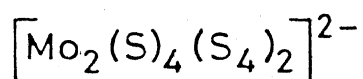
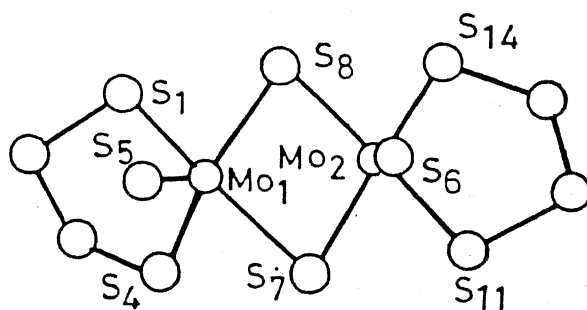
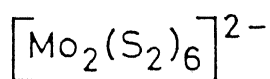
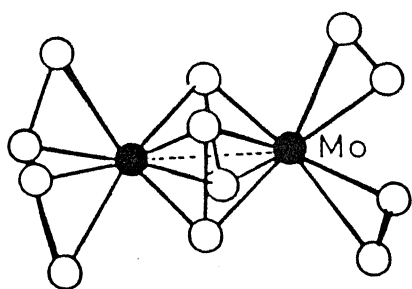
Mo CT bands are lower in energy than the $S_t \rightarrow$ Mo CT bands [67].

For disulfur complexes of the structure $M \begin{array}{c} \diagup S \diagdown \\ | \\ S \end{array} M$ the corresponding absorption band is expected to occur at higher energy because both π^* orbitals of the ligand interact strongly with the metals [66]. The band maxima of few representative examples are given in Table 1.5.

X-ray studies :

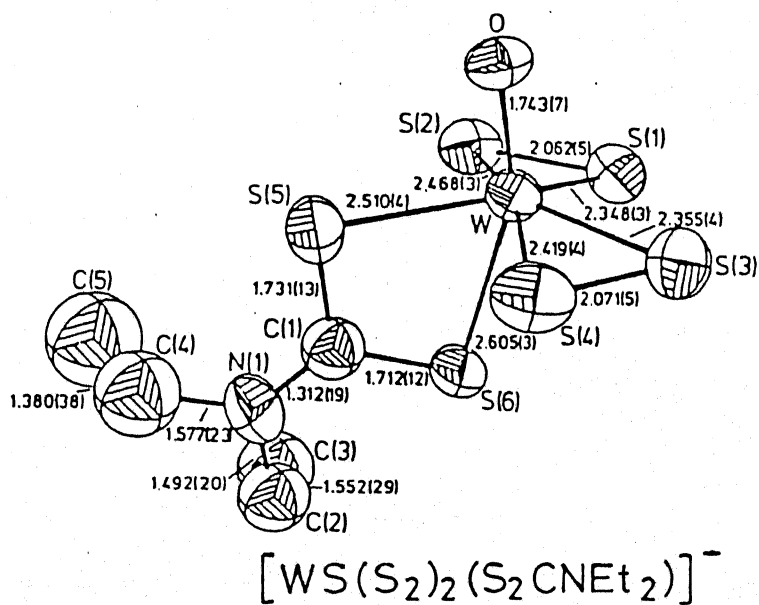
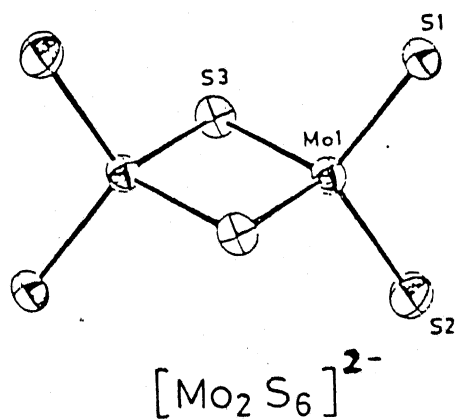
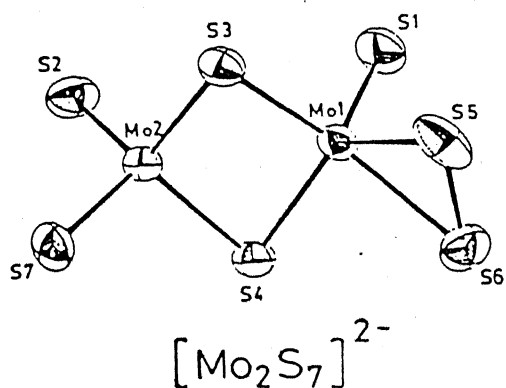
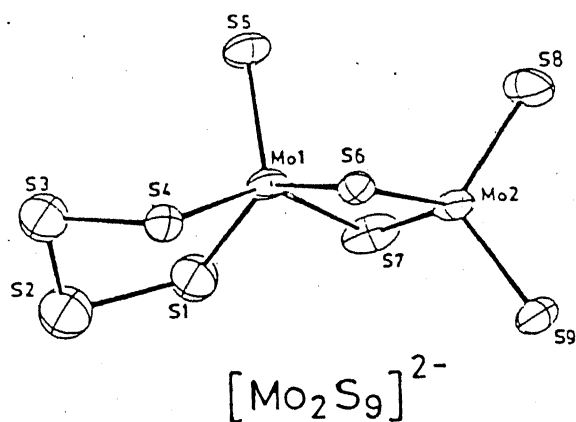
In a single-crystal study, ammonium tetrathiomolybdate has been shown to be isomorphous with β - K_2SO_4 and hence $[MoS_4]^{2-}$ ion is tetrahedral [68]. A full structure determination of $(NH_4)_2WS_4$ has shown that it consists of discrete undistorted tetrahedral $[WS_4]^{2-}$ anions [69].

One of the structural isomers $[(NH_4)_2Mo_2(S_2)_6] \cdot 2H_2O$ incorporates only $(S_2)^{2-}$ ligands [34]. Two of the $(S_2)^{2-}$ ligands bridge the two Mo atoms and four of the $(S_2)^{2-}$ ligands are bonded to a single Mo atom [Fig. 1.1]. The coordination geometry about each of the Mo atom is distorted dodecahedral. A second structural isomer of $[Mo_2S_{12}]^{2-}$ contains a syn- $Mo_2S_2(\mu-S)_2^{2+}$ core coordinated by two bidentate tetrasulfido $(S_4)^{2-}$ ligands [47]. The coordination geometry about the molybdenum is best described as that of two square pyramids sharing a common basal edge as shown in figure 1.1.



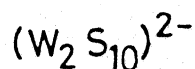
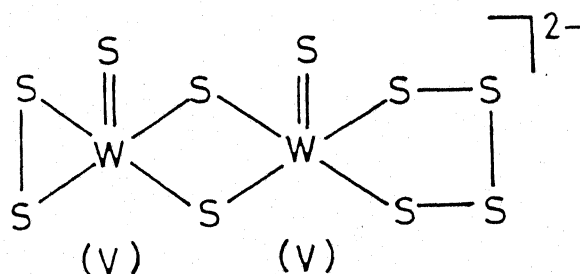
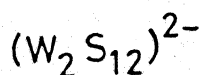
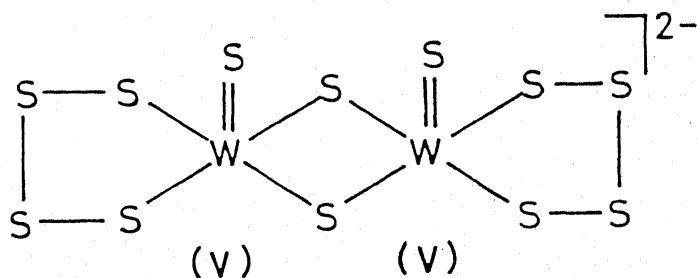
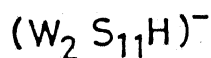
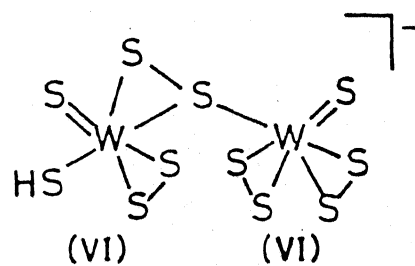
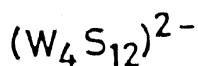
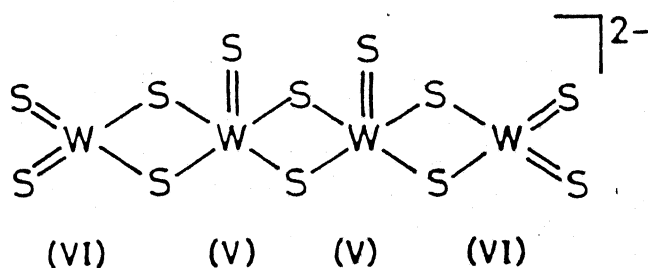
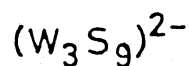
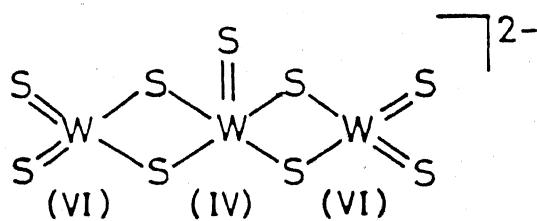
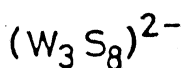
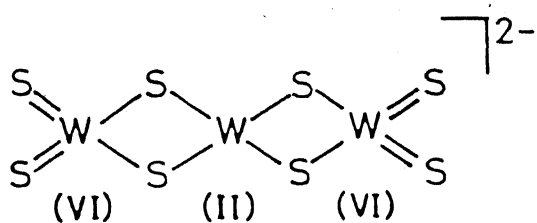
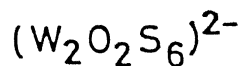
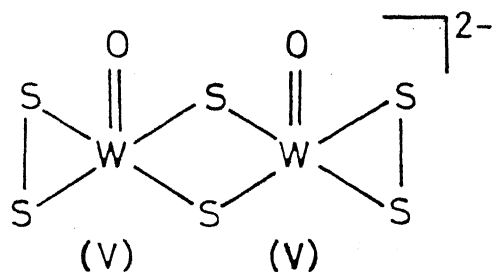
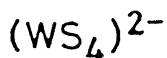
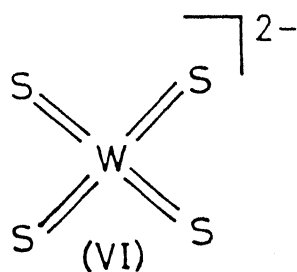
STRUCTURE TYPES OF SOME MOLYBDENUM-SULFIDO ANIONS.

FIG. 1.1



CRYSTAL STRUCTURES

FIG. 1.2



STRUCTURE TYPES OF TUNGSTEN-SULFIDO ANIONS

Table 1.6 Bond Distances in Some M-S (M = Mo, W) Complexes in Å

Compound	(S-S)	(M-S _b)	M---M	Ref
[MoO(S ₂)(S ₂ CNet ₂) ₂]	2.020	---	---	87
[WS(S ₂)(S ₂ CNet ₂) ₂]	2.208	---	---	32
(Et ₂ NH ₂)[WO(S ₂) ₂ (S ₂ CNet ₂)]	---	2.344	---	58
[Mo ₂ O ₂ (μ-S) ₂ (S ₂) ₂] ²⁻	2.080	2.825	2.830	52
[Mo ₂ OS(μ-S) ₂ (S ₂) ₂] ²⁻	2.058 2.078	2.307 2.319	2.821	24
[Mo ₂ S ₂ (μ-S) ₂ (S ₂) ₂] ²⁻	2.051 2.072	2.314 2.306	2.802 3.082	14
[Mo ₂ S ₆] ²⁻	---	2.298	2.856	33
[Mo ₂ S ₇] ²⁻	2.123	2.326	2.848	33
[Mo ₂ S ₄ (S ₄)(S ₂)] ²⁻	2.071	2.342	2.837	12
[W ₂ S ₂ (μ-S) ₂ (S ₄) ₂] ²⁻	2.930	2.320	2.836	47
[W ₂ S ₂ (μ-S) ₂ (WS ₄) ₂] ²⁻	---	2.334	2.912	28
[MoS(S ₄) ₂] ²⁻	2.166	2.331	---	31
[Mo(S)(MoS ₄)(S ₄)] ²⁻	2.015	2.370	2.859	33
[Mo(S)(MoS ₄) ₂] ²⁻	---	2.086	2.882 3.047	53
[WS(WS ₄) ₂] ²⁻	---	2.070	2.871	53
[W(WS ₄) ₂] ²⁻	---	2.338	2.870	29

Another cluster anion which contains only molybdenum and sulfur is $(\text{NH}_4)_2[\text{Mo}_3\text{S}(\text{S}_2)_6] \cdot n\text{H}_2\text{O}$ [36, 38]. The structure of this compound consists of discrete $[\text{Mo}_3\text{S}_{13}]^{2-}$ units. The cluster has three Mo atoms at the vertices of a triangle with a unique S atom above its center. There are bridging as well as terminal $(\text{S}_2)^{2-}$ ligands, both lying above and below the Mo_3 plane. Each Mo is coordinated to one terminal and two bridging $(\text{S}_2)^{2-}$ ligands as well as two other Mo atoms. (Fig. 1.1).

The complex $[\text{Mo}_2\text{S}_7]^{2-}$ assumes a distorted square-pyramidal arrangement where the terminal sulfido ligand occupies the apical position [33]. One S_2^{2-} ligand and one $[\text{MoS}_4]^{2-}$ ligand occupy the equatorial positions (Fig. 1.2). A few representative examples of the structure types of Mo and W sulfido anions are presented in figures 1.1 - 1.3 and the M-S bond distances of some complexes are listed in Table 1.6.

CHAPTER 2

SCOPE OF THE WORK

The chemistry of thiomolybdates and thiotungstates constitutes an important area of inorganic molybdenum-sulfur chemistry. As far as Fe-Mo-S chemistry is concerned, a number of structural types have been generated by binding one or two Fe(II) fragments to $[\text{MoS}_4]^{2-}$ with the formation of $\{\text{Mo} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{Fe} \end{array} \}$ units [70-72]. Ammonium tetrathiomolybdate has a deep red color when freshly prepared and is stable indefinitely in a dry inert atmosphere. But it is a common observation that in the laboratory atmosphere it acquires a mauve-brown tinge on standing. It would be of interest to know the reason behind this color change. It is also worth exploring whether the color change is influenced by light, heat or external oxidant like atmospheric oxygen.

As seen in the previous chapter, acidification of $[\text{MoS}_4]^{2-}$ ion results in the formation of $[\text{Mo}_2\text{OS}_7]^{2-}$ with the liberation of H_2S [24]. Two mechanisms have been put forth, one involving proton and the other suggesting the involvement of oxygen. Proton can function as an external oxidant by accepting electron or O_2 might accept the extra electron formed in the process of electron transfer across $\{\text{Mo}=\text{S}\}$ bond. The role of external oxidant in such processes needs clarification. Furthermore, the subtle difference in the

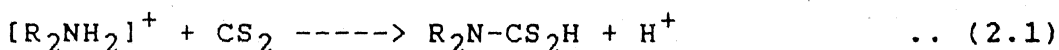
reactivity between $[\text{MoS}_4]^{2-}$ and $[\text{MoOS}_3]^{2-}$ can be addressed by observing the reactivity of $[\text{MoOS}_3]^{2-}$ under identical conditions.

As described in the earlier chapter, some of the electron transfer reactions take place across $\{\text{Mo}=\text{S}\}$ bond only when protonated cationic salts of $[\text{MoS}_4]^{2-}$ are used [53]. It would be interesting to study the relationship between different protonated salts of $[\text{MoS}_4]^{2-}$ and $[\text{MoOS}_3]^{2-}$ and their reactivity under aerobic as well as anaerobic conditions. Even thermal reactions sometimes cause electron transfer across $\{\text{Mo}=\text{S}\}$ bond, so it would be worthwhile to see the reaction of these salts even in the solid state under aerobic conditions.

$[\text{WS}_4]^{2-}$, in acid medium, under the catalytic influence of Mn^{2+} gives $[\text{W}_2\text{S}_{11}]^{2-}$ whereas $[\text{MoS}_4]^{2-}$ produces $[\text{Mo}_3\text{S}_9]^{2-}$ under identical conditions [25]. $[\text{WS}_4]^{2-}$ has also been refluxed with sulfur and then the resulting solution has been acidified to produce $[\text{W}_2\text{S}_{11}\text{H}]^-$ [26]. The reaction of elemental sulfur with $[\text{MoS}_4]^{2-}$ to yield $[\text{MoS}_9]^{2-}$ is well documented [31, 43, 44]. Contrary to this, similar reaction with $[\text{WS}_4]^{2-}$ at elevated temperature produces $[\text{W}_2\text{S}_{12}]^{2-}$ [47]. It would be interesting to know the reaction of $[\text{MoS}_4]^{2-}$ under the influence of both elemental sulfur and proton. The proton source could be externally provided or

the reaction can be carried out using protonated cationic salts of the corresponding tetrathiomallates. It would be worthwhile to examine the corresponding oxotrithiomallates under identical conditions.

The interaction of coordinated $(S_2)^{2-}$ and $(S_4)^{2-}$ with CS_2 to produce $(CS_4)^{2-}$ units has been well documented [73]. The possibility of forming a dithiocarbamate ligand in situ is a unique feature when protonated cationic salts are used.



Thus the reaction of protonated cationic salts of $[MoS_4]^{2-}$ and $[MoOS_3]^{2-}$ with CS_2 may open new avenues as exciting synthetic strategy. The difference in the reactivity between protonated cationic and non protonated cationic salts of these thiomolybdates would lead to interesting observations.

Although in general, $[MoOS_3]^{2-}$ and $[MoS_4]^{2-}$ have similar reactivity, there are certain reactions wherein their reactivity differs significantly. For e.g. the bimetallic Fe-Mo complex, $[Cl_2Fe(\mu-S)_2Mo(O)(S_2)]^{2-}$ having bridging sulfido, disulfido and terminal oxo ligands could be isolated by reacting $[MoOS_3]^{2-}$ with sulfur and $FeCl_2$ [74]. However, attempts to isolate the all sulfur compound $[(S_2)(S)Mo(\mu-S)_2FeCl_2]$ by using $[MoS_4]^{2-}$ have failed.

When $[\text{MoOS}_8]^{2-}$ is reacted with activated acetylenes such as DMAD (dimethyl acetylene dicarboxylate), the penta coordinated $[\text{MoO}(\text{S}_2\text{C}_2\text{COOMe})_2]^{2-}$ complex is obtained. But with $[\text{MoS}_9]^{2-}$, the hexa coordinated monomeric complex, $[\text{Mo}(\text{S}_2\text{C}_2(\text{COOMe})_2)_3]^{2-}$ is isolated under N_2 atmosphere and the dimer $[\text{Mo}_2\text{S}_2(\text{S}_2\text{C}_2(\text{COOMe})_2)_4]^{2-}$ is formed if the reaction is done in air [50]. Thus, the trend in the reactivity between tetrathiometalates and oxotriithiometalates which is important from the coordination chemistry point of view, may be studied.

The isolated complexes, if any, using the above mentioned strategies, could be subjected to modern physico-chemical techniques for the elucidation of their structure. The reactivity of the isolated compounds could also be tried with the help of existing known chemistry in the allied field. The nature of these reactions and bonding mode of the ligands may be worth investigating. Any differences in reactivity between $[\text{MoS}_4]^{2-}$ and $[\text{WS}_4]^{2-}$ could be stretched upon in the light of the involvement of Mo-S systems in biology compared to the corresponding W-S compounds.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 GENERAL CONSIDERATIONS :

All the reactions were carried out in air, unless specified otherwise. The solvents were distilled and stored over 4 Å molecular sieves before use.

3.1.1 Methods of analysis and work-up manipulations

The elements carbon, hydrogen and nitrogen were analyzed by standard microanalytical techniques at the Indian Institute of Technology, Kanpur. Sulfur was estimated as BaSO_4 and the procedure is as follows:

Sulfur

About 150 mg of the sulfur containing compound was oxidized with an excess of alkaline bromine water. The excess bromine was evaporated off by warming the solution slowly. To the resulting solution, hydrochloric acid was added slowly and the liberated bromine was again evaporated off. The solution was filtered and the sulfate in the filtrate was estimated gravimetrically as barium sulfate by the standard method [75].

3.2 SYNTHESSES OF THE STARTING MATERIALS :

3.2.1 Preparation of ammonium tetrathiomolybdate [76, 77]

Ammonium heptamolybdate (5.0 g) was dissolved in a mixture of conc. ammonium hydroxide (30 mL) and water (10 mL) and the solution filtered. Hydrogen sulfide gas was passed rapidly into the filtrate. The color of the solution initially changed to

yellow and gradually to red. After passing hydrogen sulfide gas for 30 min, red crystals started depositing. The gas flow was stopped and the deep red solution was cooled at 0°C for 20 min. Red crystals of ammonium tetrathiomolybdate were isolated by filtration, washed with a little cold water, ethanol and ether and dried in vacuo. Yield 80% .

The compound gave a characteristic band at 480 cm^{-1} in the IR spectrum due to ν_{as} (Mo-S) vibration.

3.2.2 Preparation of ammonium tetrathiotungstate [77]

Sodium tungstate (5.0 g) was dissolved in a mixture of conc. ammonium hydroxide (40 mL) and water (10 mL). The solution was warmed to 60°C and hydrogen sulfide gas was bubbled into it for 9 h by maintaining the temperature at 60°C . The solution was cooled at 10°C to yield the orange-yellow ammonium tetrathiotungstate. The product was filtered, washed with a little amount of cold water, ethanol and ether and dried in vacuo. Yield 50% .

The IR spectrum of the compound showed a characteristic band at 460 cm^{-1} due to ν_{as} (W-S) vibration.

3.2.3 Preparation of cesium oxotrichiomolybdate [77]

Ammonium heptamolybdate (5.0 g) and cesium chloride (15.0 g) were dissolved in a mixture of water (20 mL) and conc. ammonium hydroxide (15 mL). Conc. acetic acid (8 mL) was added to this solution and hydrogen sulfide gas was bubbled into it for 15 min at room temperature. The gas flow was stopped as soon as orange-red crystals started appearing. The solution was cooled

in an ice-bath for 5 min and the orange-red crystals were isolated by filtration. The crystals were washed with a little amount of cold water, followed by ethanol and finally with ether and dried under vacuum. Yield 78% .

The IR spectrum of the compound showed characteristic bands at 862 cm^{-1} and 480 cm^{-1} due to $\nu_{\text{as}}(\text{Mo-O})$ and $\nu_{\text{as}}(\text{Mo-S})$ vibrations, respectively.

3.2.4 Preparation of ammonium oxotrithiotungstate [77]

Sodium tungstate (5.0 g) was dissolved in a mixture of water (5 mL) and conc. ammonium hydroxide (20 mL) and the solution was filtered. Hydrogen sulfide gas was bubbled rapidly into the filtrate for 25 min at room temperature. A small amount of ammonium dioxodithiotungstate separated out. The reaction mixture was filtered rapidly into ice cold isopropanol (500 mL) and the product separated out as a yellow powder. The yellow powder was isolated by filtration washed well with isopropanol and ether and dried under vacuum. Yield 74% .

The IR spectrum of the compound gave bands at 860 cm^{-1} and 470 cm^{-1} due to $\nu_{\text{as}}(\text{W-O})$ and $\nu_{\text{as}}(\text{W-S})$ vibrations, respectively.

3.2.5 Preparation of tetraphenylphosphonium or arsonium thiometallates

The tetraphenylphosphonium or arsonium thiometallates $(\text{XPh}_4)_2[\text{MO}_n\text{S}_{4-n}]$ $\text{X} = \text{P, As}$; $\text{M} = \text{Mo, W}$; $n = 0, 1$) were prepared by cation exchange from an aqueous solution of the ammonium or cesium salt of the thiometallate and the respective $(\text{XPh}_4)^+$ salt.

3.2.6 Preparation of ammonium dioxodithiomolybdate [77]

Sodium molybdate (5 g) was dissolved in 25% ammonia solution (20 mL) and the solution was cooled in ice. H_2S was passed over the surface of the ice-cold solution for 10 min. Orange-yellow crystalline dioxodithiomolybdate separated out of the solution. The crystals were filtered, washed with ice-cold water, alcohol and ether and dried under vacuum. Yield ~60% .

The compound gave characteristic bands in its IR spectrum at 861, 840, 470 and 450 cm^{-1} .

3.2.7 Preparation of diethylammonium tetrathiomolybdate

Molybdic acid (5 g, 0.03 mol) was stirred in a mixture of water (10 mL) and diethylamine (15 mL) for 1 h. The solution was filtered and H_2S gas was passed rapidly into the solution for 30 min. at room temperature. The red crystals that formed were filtered, washed with isopropanol and ether and dried in vacuo. Yield 76% .

Anal. Calcd. for

$\text{C}_8\text{H}_{24}\text{N}_2\text{MoS}_4$: C, 25.81; H, 6.45; N, 7.53; S, 34.41

Found : C, 25.72; H, 6.38; N, 7.58; S, 34.49

3.2.8 Preparation of dimethylammonium tetrathiomolybdate

This compound was prepared by following the same procedure as mentioned above for its ethyl analog except that 40% dimethylamine solution (20 mL) was used in the place of diethylamine. Yield 78% .

Anal. Calcd. for

$C_4H_{16}N_2MoS_4$: C, 15.19; H, 5.06; N, 8.86; S, 40.51

Found : C, 15.11; H, 5.12; N, 8.80; S, 40.41

3.2.9 Preparation of dipropylammonium tetrathiomolybdate

The same procedure as mentioned earlier for the synthesis of the ethyl analog was followed for the isolation of this compound. Dipropylamine (15 mL) was used instead of diethylamine. Yield 70% .

Anal. Calcd. for

$C_{12}H_{32}N_2MoS_4$: C, 33.65; H, 7.47; N, 6.54; S, 29.91

Found : C, 33.55; H, 7.39; N, 6.49; S, 29.98

3.2.10 Preparation of piperidinium tetrathiomolybdate

This compound was also prepared by following the same procedure as mentioned earlier for its ethyl analog except that piperidine (15 mL) was used in the place of diethylamine. Yield 75% .

Anal. Calcd. for

$C_{10}H_{24}N_2MoS_4$: C, 30.30; H, 6.06; N, 7.07; S, 32.32

Found : C, 30.22; H, 6.17; N, 7.13; S, 32.28

3.2.11 Preparation of diethylammonium oxotrithiomolybdate [45]

Molybdic acid (1.62 g, 0.01 mol) was stirred in a mixture of water (10 mL) and diethylamine (10 mL) for 1 h. The resulting solution was filtered and H_2S gas was passed over the surface of the filtrate for 5 min. at room temperature. Iso-propanol (30 mL) and ether (10 mL) were added and the solution was kept for 2h

at 0°C to yield red-orange crystals. The crystals were filtered, washed with a little ice-cold water, isopropanol and ether and dried under vacuum. Yield 70% .

Anal. Calcd. for

$C_8H_{24}N_2MoOS_3$: C, 26.97; H, 6.74; N, 7.87; S, 26.97

Found : C, 26.92; H, 6.51; N, 7.68; S, 26.98

3.2.12 Preparation of dimethylammonium oxotrithiomolybdate

The same procedure as mentioned above for the synthesis of diethylammonium oxotrithiotungstate was followed for the preparation of this compound except that dimethylamine was used in the place of diethylamine. Yield 70% .

Anal. Calcd. for

$C_4H_{16}N_2MoOS_3$: C, 16.00; H, 5.33; N, 9.33; S, 32.01

Found : C, 15.41; H, 5.83; N, 9.68; S, 31.87

3.2.13 Preparation of dipropylammonium oxotrithiomolybdate

The same procedure as mentioned earlier for the synthesis of diethylammonium oxotrithiotungstate was followed for the preparation of this compound except that dipropylamine was used in the place of diethylamine. Yield 70% .

Anal. Calcd. for

$C_{12}H_{32}N_2MoOS_3$: C, 34.96; H, 7.77; N, 6.79; S, 23.30

Found : C, 34.79; H, 8.03; N, 6.18; S, 23.17

3.2.14 Preparation of piperidinium oxotrithiomolybdate

The same procedure as mentioned earlier for the synthesis of diethylammonium oxotrithiotungstate was followed for the preparation of this compound except that piperidine was used in the place of diethylamine. Yield 70% .

Anal. Calcd. for

$C_{10}H_{24}N_2MoOS_3$: C, 31.58; H, 6.32; N, 7.37; S, 25.27

Found : C, 31.94; H, 6.61; N, 7.02; S, 25.10

3.2.15 Preparation of tetraethylammonium oxobis(tetrasulfido)

molybdenum IV; $(Et_4N)_2[MoO(S_4)_2]$ [45]

A solution of $(Et_2NH_2)MoOS_3$ (356 mg, 1 mmol) in CH_3CN (20 mL) was stirred with Et_4NBr (420 mg, 2mmol) and elemental sulfur (160 mg, 5 mmol) for 30 min and left overnight to yield a golden yellow crystalline product. The product was filtered, washed with water, ethanol, carbondisulfide and ether and dried under vacuum. Yield 88% .

Anal. Calcd. for

$C_{16}H_{40}N_2MoOS_8$: C, 30.58; H, 6.37; N, 4.46; S, 40.77

Found : C, 30.57; H, 6.36; N, 4.45; S, 40.76

3.3 AGING OF AMMONIUM TETRATHIOMOLYBDATE IN AIR : [78]

Powdered samples of $(NH_4)_2MoS_4$ was stored in a dessicator over fused $CaCl_2$ and in the laboratory atmosphere (temperature 28 ± 2 °C and humidity 70 ± 5 %) and the surface color was monitored from time to time. The sample stored at the laboratory atmosphere acquired a mauve-brown tinge in a week. The sample was then extracted with dichloromethane in the presence of Et_4NBr .

The solvent was then evaporated and the residue was washed with water and isopropanol. It was then recrystallized from acetonitrile / isopropanol.

The sample in the dessicator changed to the same color in about six months which was also worked up in the same way as mentioned above.

Anal. Calcd. for

$C_{16}H_{40}N_2Mo_2O_2S_6$: C, 28.41; H, 5.92; N, 4.14; S, 28.41

Found : C, 28.10; H, 5.30; N, 4.78; S, 28.29

3.4 THERMAL REACTION OF AMMONIUM TETRATHIOMOLYBDATE IN AIR :

$(NH_4)_2MoS_4$ (260 mg, 1 mmol) was added to a melt of Et_4NBr (504 mg, 2.4 mmol) at $105 \pm 5^\circ C$ and a current of dry air was passed over the surface for 10 min. The resulting mass was extracted in dichloromethane. The dichloromethane extract was worked up in the same way as described above to yield a microcrystalline product. Yield 70% .

Anal. Calcd. for

$C_{16}H_{40}N_2Mo_2OS_7$: C, 27.75; H, 5.78; N, 4.05; S, 32.38

Found : C, 27.36; H, 5.28; N, 4.83; S, 32.12

3.5 INTERACTION OF THIOMOLYBDATES AND THIO TUNGSTATES WITH SULFUR IN THE PRESENCE OF PROTON : [79]

3.5.1 Preparation of $(AsPh_4)_2[Mo_2(S)_2(\mu-S)(S_2)_4] \cdot CH_3CN$

To a solution of tetraphenylarsonium tetrathiomolybdate (370 mg, 0.37 mmol) in acetonitrile (10 mL), sulfur (20 mg, .62 mmol) was added. After stirring the solution for 2 min. 0.04 mL of glacial acetic acid was added into the mixture, whereby the

orange-red color of the solution changed to dark brown. The solution was stirred for 5 more min. , filtered and cooled in the refrigerator to produce brown crystals. The crystals were filtered, washed with ether and dried under vacuum. Yield 25% .

Anal. Calcd. for

$C_{50}H_{43}As_2NMo_2S_{11}$: C, 44.42; H, 3.18; N, 1.04; S, 26.05

Found : C, 44.10; H, 3.00; N, 1.01; S, 26.00

3.5.2 Preparation of $(PPh_4)_2[Mo_2(S)_2(\mu-S)(S_2)_4] \cdot CH_3CN$

This compound was prepared by following the same procedure as mentioned above for its tetraphenylarsonium analog. Tetraphenylphosphonium tetrathiomolybdate was used in the place of $(AsPh_4)_2MoS_4$. Yield 25% .

Anal. Calcd. for

$C_{50}H_{43}P_2NMo_2S_{11}$: C, 47.51; H, 3.41; N, 1.11; S, 27.87

Found : C, 47.28; H, 3.27; N, 1.04; S, 27.59

3.5.3 Preparation of $[(C_2H_5)_2NH_2]_2[Mo_2(S)_2(\mu-S)(S_2)_4]$

Method A

Diethylammonium tetrathiomolybdate (372 mg, 1 mmol) was dissolved in DMF (5 mL) and sulfur (64 mg, 2 mmol) was added. The solution was stirred overnight under nitrogen atmosphere and filtered. Isopropanol (150 mL) and petroleum ether [40-60 °C] (60 mL) were added into the clear filtrate and the solution was cooled at 5 °C for 20 h. under inert atmosphere. The brown crystals that separated out were filtered, washed with isopropanol and petroleum ether and dried under vacuum. Yield 25% .

Method B

Ammonium tetrathiomolybdate (260 mg, 1mmol) was dissolved in DMF (5 mL) and diethylamine (3 mL) was added. Sulfur (64 mg, 2 mmol) was added into the clear solution and the reaction mixture was purged with nitrogen and stirred overnight. It was then filtered, and isopropanol (150 mL) and petroleum ether (60 mL) were added and kept at 5°C under nitrogen atmosphere overnight. The brown crystals which were formed, were filtered off, washed with isopropanol and petroleum ether and dried under vacuum. Yield 25% .

Anal. Calcd. for

$C_8H_{24}N_2Mo_2S_{11}$: C, 13.88; H, 3.47; N, 4.05; S, 50.88

Found : C, 13.79; H, 3.41; N, 3.99; S, 50.75

3.5.4 Preparation of $(AsPh_4)_2[Mo_2(O)_2(\mu-S)(S_2)_4].CH_3CN$

Tetraphenylarsonium oxotrichiomolybdate (210 mg, 0.215 mmol) was dissolved in acetonitrile (5 mL) and elemental sulfur (10 mg, 0.31 mmol) was slowly added with stirring. A solution of glacial acetic acid (.04 mL) in methanol (3 mL) was added and the reaction mixture was stirred for 5 min. The resulting solution was filtered and kept at 5 °C. The brown crystals that separated out were filtered off and washed with ether and dried in vacuo. Yield 45% .

Anal. Calcd. for

$C_{50}H_{43}NAS_2Mo_2O_2S_9$: C, 45.98; H, 3.29; N, 1.06; S, 21.84

Found : C, 45.30; H, 3.18; N, 0.99; S, 22.09

3.5.5 Preparation of $(\text{PPh}_4)_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]\cdot\text{CH}_3\text{CN}$

The procedure employed for the preparation and isolation of this complex is identical to that of its tetraphenylarsonium analog except that tetraphenylphosphonium oxotrichiomolybdate was used. Yield 43% .

Anal. Calcd. for

$\text{C}_{50}\text{H}_{43}\text{NP}_2\text{Mo}_2\text{O}_2\text{S}_9$: C, 48.75; H, 3.49; N, 1.14; S, 23.40

Found : C, 48.54; H, 3.26; N, 1.03; S, 23.26

3.5.6 Preparation of $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$

Ammonium dioxodithiomolybdate (230 mg, 1 mmol) was dissolved in DMF (5 mL) and dimethylamine (3 mL) was added. Elemental sulfur (96 mg, 3 mmol) was added to the solution with stirring under nitrogen atmosphere. The stirring was continued overnight and the solution was filtered. Isopropanol (150 mL) and petroleum ether (40-60 °C) (60 mL) were added into the clear filtrate and the solution was cooled at 0 °C to yield brown crystals. The crystals were washed with isopropanol and petroleum ether and dried under vacuum. Yield 20% .

Anal. Calcd. for

$\text{C}_4\text{H}_{16}\text{N}_2\text{Mo}_2\text{O}_2\text{S}_9$: C, 7.95; H, 2.59; N, 4.64; S, 47.69

Found : C, 7.87; H, 2.59; N, 4.61; S, 47.62 .

3.5.7 Preparation of $(\text{AsPh}_4)_2[\text{W}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]\cdot\text{CH}_3\text{CN}$

Tetraphenylarsonium tetrathiomolybdate (260 mg 0.24 mmol) was dissolved in CH_3CN (5 mL), and sulfur (11mg, 0.34 mmol) was added into it. The solution was stirred for 5 min and glacial acetic acid (0.1 mL) in methanol (5 mL) were added to the

reaction mixture. After stirring for 1 h the reaction mixture was filtered and refrigerated overnight to yield brown microcrystals. The crystals were filtered, washed with ether and dried in vacuo. Yield 25% .

Anal. Calcd. for

$C_{50}H_{43}NaS_2W_2S_{11}$: C, 39.30; H, 2.82; N, 0.92; S, 23.05

Found : C, 39.10; H, 2.59; S, 23.41; N, 0.91 .

3.5.8 Preparation of $(PPh_4)_2[W_2(S)_2(\mu-S)(S_2)_4].CH_3CN$

This compound was prepared by following the same procedure as mentioned above for its tetraphenylarsonium analog. Tetraphenylphosphonium tetrathiotungstate was used in the place of tetraphenylarsonium tetrathiotungstate. Yield 25% .

Anal. Calcd. for

$C_{50}H_{43}NP_2W_2S_{11}$: C, 41.71; H, 2.99; N, 0.97; S, 24.47

Found : C, 41.52; H, 2.71; N, 0.88; S, 24.32

3.5.9 Preparation of $(AsPh_4)_2[W_2(O)_2(\mu-S)(S_2)_4].CH_3CN$

Tetraphenylarsonium oxotrichthiotungstate (230 mg, 0.24mmol) was dissolved in acetonitrile (7 mL). To this clear solution, elemental sulfur (10 mg, 0.31 mmol) was added. A green tinge developed which soon became dark brown. Glacial acetic acid (0.1 mL) in methanol (5 mL) was added into the mixture whereby the solution became orange-red. After stirring for 1 h, the solution was filtered and cooled (0 °C) to produce orange-red crystals which were washed with ether and dried under vacuum. Yield 36% .

Anal. Calcd. for

$C_{50}H_{43}As_2NW_2O_2S_9$: C, 40.15; H, 2.88; N, 0.94; S, 19.27

Found : C, 39.91; H, 2.68; N, 1.03; S, 20.59

3.5.10 Preparation of $(PPh_4)_2[W_2(O)_2(\mu-S)(S_2)_4] \cdot CH_3CN$

The procedure employed for the preparation and isolation of this complex is identical to that of its tetraphenylarsonium analog except that tetraphenylphosphonium oxotrithiomolybdate was used. Yield 21% .

Anal. Calcd. for

$C_{50}H_{43}NW_2O_2S_9$: C, 42.65; H, 3.06; N, 0.96; S, 20.47

Found : C, 42.49; H, 3.12; N, 0.89; S, 20.25.

3.6 REACTION OF THIOMOLYBDATES WITH SULFUR AND ACTIVATED ACETYLENES :

3.6.1 Preparation of $(Et_4N)_2[Mo(S_2C_2(COPh)_2)_3]$

Ammonium tetrathiomolybdate (86 mg, 0.33 mmol) was dissolved in DMF (10 mL) and Et_4NBr (210 mg, 1 mmol), sulfur (32 mg, 1 mmol) and dibenzoyl acetylene (234 mg, 1 mmol) were added and the reaction mixture was stirred vigorously for 3 h. The dark green solution was filtered and ethanol (15 mL) was added and the solution kept overnight at 5 °C. The kelly green crystals were isolated by filtration, washed with ethanol and ether and dried under vacuum. Yield 45% .

Anal. Calcd. for

$C_{61}H_{70}N_2MoS_6O_3$: C, 62.78; H, 6.00; N, 2.40; S, 16.47

Found : C, 62.39; H, 5.49; N, 2.15; S, 16.18

3.6.2 Preparation of $(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]$ [45]

$(Et_4N)_2MoO(S_4)_2$ (314 mg, 0.5 mmol) was dissolved in DMF (5 mL) by warming on a water bath for 10 min. Dibenzoyl acetylene (234 mg, 1 mmol) was added to this solution and the solution was warmed for 10 more min over water bath. The solution was cooled and isopropanol (50 mL) was added resulting in the formation of an oily mass. The oily mass so obtained was dissolved in CH_3CN (10 mL), and then absolute ethanol (20 mL) and isopropanol (10 mL) were added to it. Keeping the solution for 2 days at room temperature resulted in the formation of a dark brown crystalline product which was washed with ethanol and ether and dried under vacuum. Yield (190 mg) 39% .

Anal. Calcd. for

$C_{48}H_{60}N_2MoS_4O_5$: C, 59.50; H, 6.19; N, 2.89; S, 13.22

Found : C, 59.62; H, 6.10; N, 2.80; S, 13.28

3.7 REACTION OF THIOMOLYBDATES WITH CARBONDISULFIDE :

3.7.1 Preparation of $(PPh_4)_2[MoO(CS_3)(CS_4)]$

A solution of Cs_2MoOS_3 (474 mg, 1 mmol) in acetonitrile (15 mL) was stirred with PPh_4Br (840 mg, 2 mmol) for 3 min. Carbon-disulfide (2 mL) was then added dropwise to the solution and the stirring was continued under nitrogen for 2 h. The reaction mixture was then filtered and isopropanol (50 mL) was added slowly with swirling. The shining greenish-brown crystals, which separated from the solution were filtered and washed with isopropanol and ether and dried in vacuo. Yield 40%.

Anal. Calcd. for

$C_{50}H_{40}P_2MoOS_7$: C, 57.81; H, 3.85; S, 21.58

Found : C, 57.71; H, 3.68; S, 21.37

3.7.2 Preparation of $(PPh_4)_2[Mo_2(\mu-S)_2(CS_3)_4]$

Ammonium tetrathiomolybdate (260 mg, 1 mmol) and PPh_4Br (839 mg, 2 mmol) were stirred in degassed acetonitrile (15 mL) under nitrogen atmosphere. Carbondisulfide (1 mL) was added to this solution under nitrogen atmosphere and the contents of the flask were stirred overnight. A brown microcrystalline product was thrown out of the solution. The product was washed well with water, iso-propanol, and ether and dried under vacuum. Yield 35%.

Anal. Calcd. for

$C_{52}H_{40}P_2Mo_2S_{14}$: C, 45.69; H, 2.93; S, 32.80

Found : C, 45.24; H, 2.80; S, 32.09 .

3.7.3 Preparation of $[Mo_2(\mu-S)_2(CS_3)_2(S_2CN(C_2H_5)_2)_2]$

Method A

Ammonium tetrathiomolybdate (260 mg, 1 mmol) was dissolved in DMF (10 mL) and diethylamine (2 mL) was added and the solution stirred for 1 h in air. The solution was kept in an ice-bath and carbondisulfide (1 mL) was added dropwise with stirring. The reaction mixture was poured into ice-cold water, after stirring for an additional 30 min. The brown microcrystalline product that separated out was filtered and washed well with water, isopropanol and ether successively and dried in vacuo. Yield 50%

Method B

Diethylammonium tetrathiomolybdate (372 mg, 1 mmol) and carbondisulfide (10 mL) were stirred vigorously in air overnight. The brown microcrystalline product that separated out was filtered from the carbondisulfide solution and washed well with water, isopropanol, and ether and dried in vacuum. Yield 53% .

Method C

Diethylammonium tetrathiomolybdate (372 mg, 1 mmol) was dissolved in acetonitrile (10 mL) and carbondisulfide (1 mL) was added to the above solution in drops. The solution was stirred for 4 h and then filtered. Isopropanol (15 mL) was added to the filtrate and the solution was left at 5 °C overnight. The brown microcrystalline product that had deposited was washed with isopropanol, and ether and dried in vacuo. Yield 47% .

Anal. Calcd. for

$C_{12}H_{20}N_2Mo_2S_{12}$: C, 18.75; H, 2.60; N, 3.65; S, 50.01

Found : C, 18.66; H, 2.45; N, 3.53; S, 50.53 .

3.7.4 Preparation of $[MoO(S_2)(S_2CN(C_2H_5)_2)_2]$ Method A

Ammonium dioxodithiomolybdate (228 mg, 1 mmol) in DMF (10 mL) was stirred with diethylamine (1 mL) to get a clear solution. Carbondisulfide (1 mL) was added dropwise to the above solution and the reaction mixture was stirred for 3 h, and then poured over water to give a yellow-green product. The product was separated by filtration and dried. It was dissolved in dichloromethane and passed over a silica gel column. The blue

fraction which was eluted first was collected, concentrated under reduced pressure. Addition of petroleum ether (40-60 °C) yielded a blue crystalline product. Yield 40% .

Anal. Calcd. for

$C_{10}H_{20}N_2MoOS_6$: C, 25.43; H, 4.24; N, 5.93; S, 40.68

Found : C, 25.19; H, 3.97; N, 5.69; S, 40.59 .

Method B

Diethylammonium oxotrichiomolybdate (356 mg, 1 mmol) was dissolved in DMF (10 mL) and carbondisulfide (1 mL) was added to the clear solution dropwise. The reaction mixture was stirred for 2 h and then flooded with isopropanol to give the crude product. The crude product was purified by column chromatography to give a blue colored fraction and a yellow one. The blue fraction was identified as $[MoO(S_2)(S_2CN(C_2H_5)_2)_2]$.

3.7.5 Preparation of $[Mo_2O_2(\mu-S)_2(S_2CN(C_2H_5)_2)_2]$

The same procedure as mentioned earlier (Method A or B of 3.7.4) was followed for the preparation of this dimeric complex. The crude product of the earlier reactions gave two fractions, a blue fraction and a second yellow fraction by column chromatography. The yellow fraction was concentrated under reduced pressure and petroleum ether (40-60 °C) was added in drops till it became hazy and kept at 5 °C overnight. The yellow crystals which deposited were filtered and washed with petroleum ether and dried under vacuum. Yield 30% .

Anal. Calcd. for

$C_{10}H_{20}N_2Mo_2O_2S_6$: C, 20.55; H, 3.43; N, 4.80; S, 32.88

Found : C, 20.29; H, 3.27; N, 4.53; S, 32.30 .

3.8 REACTION OF THIOMOLYBDATES IN THE PRESENCE OF EXTERNAL OXIDANTS LIKE I_2 AND $(S_2O_8)^{2-}$:

3.8.1 Preparation of $[(C_2H_5)_4N]_2[Mo_2OS(\mu-S)_2(S_2)_2]$

Diethylammonium tetrathiomolybdate (372 mg, 1 mmol) was dissolved in DMF (10 mL) and the solution was stirred in air. To this solution a pinch of iodine was added. The stirring was continued for 30 min. and then $(C_2H_5)_4NBr$ (735 mg, 3.5 mmol) was added to the reaction mixture. After stirring for 10 min the reaction mixture was flooded with isopropanol to yield a brown solid. The brown solid was purified by column chromatography over silica gel. A 30:70 mixture of acetonitrile and dichloromethane was used as the eluant. The middle band which contained the major product was collected and the solvents were evaporated slowly to yield purple needles. Yield 50% .

Anal. Calcd. for

$C_{16}H_{40}N_2Mo_2OS_7$: C, 27.75; H, 5.78; N, 4.05; S, 32.38

Found : C, 27.36; H, 5.28; N, 4.83; S, 32.12 .

3.8.2 Preparation of $[(C_2H_5)_4N]_2[Mo_2(O)_2(\mu-S)_2(S_2)_2]$

Diethylammonium oxotrichiomolybdate (372 mg, 1 mmol) in CH_3CN (15 mL) was stirred with Et_4NBr (735 mg, 3.5 mmol) and a pinch of iodine was added into the solution. The stirring was continued for 1 h and then isopropanol (25 mL) was added. The solution was left overnight to yield red-orange crystals which

were filtered, washed with isopropanol and ether and dried under vacuum. Yield 70% .

Anal. Calcd. for

$C_{16}H_{40}N_2Mo_2O_2S_6$: C, 28.41; H, 5.92; N, 4.14; S, 28.41

Found : C, 28.10; H, 5.30; N, 4.78; S, 28.29 .

3.8.3 Preparation of $(NH_4)_2[Mo_3S_{13}]$

Method A

A solution of ammonium tetrathiomolybdate (780 mg, 3 mmol) in water (5 mL) was stirred with sulfur (32 mg, 1 mmol) and ammonium persulfate (456 mg, 2 mmol) for 3 h. Ammonia solution was added to the reaction mixture and heated over a water bath for 1 h. The red product that had settled down at the bottom was filtered and washed with ethanol and ether. Yield 30% .

Anal. Calcd. for

$H_8N_2Mo_3S_{13}$: H, 1.08; N, 3.78; S, 56.22

Found : H, 1.93; N, 3.59; S, 56.11 .

Method B

Ammonium tetrathiomolybdate (780 mg, 3 mmol) was dissolved in water (5 mL). Sulfur (32 mg, 1mmol) and iodine (666 mg, 5.25 mmol) dissolved in aqueous KI solution were added to the above solution and the reaction mixture was stirred overnight. The supernatant liquid was discarded and ammonia solution (5 mL) saturated with H_2S gas was added and the contents of the flask were stirred for 2 h. The red solution was digested on a water bath for 15 min and the red crystals that formed, were filtered, washed with ethanol and ether and dried under vacuum. Yield 28%

3.8.4 Preparation of $[(C_2H_5)_4N]_2[Mo_2(O)_2(\mu-S)_2(S_2)_2]$

A solution of Et_4NBr (1.05 g, 5 mmol) was added to the filtrate obtained from the above preparation (method B 3.8.3). The red-orange precipitate was collected by filtration, washed with water, ethanol and ether and recrystallized from acetonitrile / isopropanol. Yield 35%

Anal. Calcd. for

$C_{16}H_{40}N_2Mo_2O_2S_6$: C, 28.41; H, 5.92; N, 4.14; S, 28.41

Found : C, 28.10; H, 5.30; N, 4.78; S, 28.29 .

3.9 OTHER REACTION :

3.9.1 Preparation of $[MoOCl(S_2CN(C_2H_5)_2)_2]$

Molybdic acid (324 mg, 2 mmol) was dissolved in conc. HCl (30 mL) and hydrazine hydrate (1 mL) was added in drops over a period of 15 min. The solution was heated on a water bath for 30 min. The green solution was filtered and $Na[S_2CN(C_2H_5)_2] \cdot 3H_2O$ (901 mg, 4 mmol) dissolved in absolute ethanol was added in drops. The crude brown product which separated out was filtered, washed with absolute ethanol several times and then ether and dried in vacuo. The dried product was recrystallized from a mixture of dichloromethane and petroleum ether. Yield 65% .

Anal. Calcd. for

$C_{10}H_{20}N_2MoOClS_4$: C, 27.06; H, 4.51; N, 6.31; S, 28.87

Found : C, 27.26; H, 4.09; N, 6.52; S, 28.23 .

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Structural aspects of the synthesized complexes :

4.1.1 Infrared Spectra

The infrared spectra of the complexes synthesized in this work, were recorded on a Perkin Elmer model-580 infrared grating spectrophotometer. The samples were prepared as CsI pellets and the absorption frequencies have been referenced to polystyrene bands.

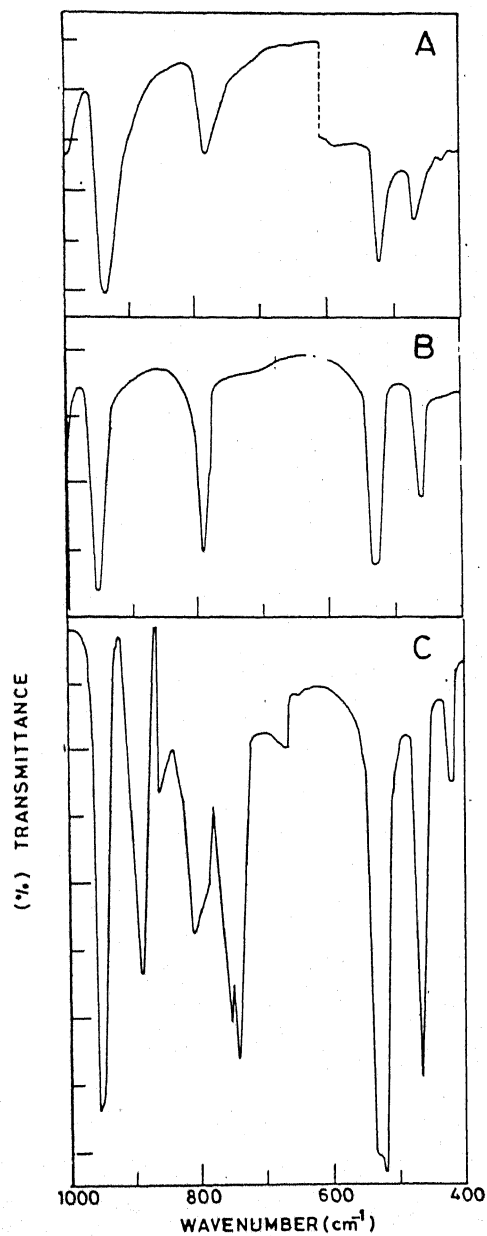
Infrared spectroscopy can play a very helpful role in determining the structure of the synthesized compounds. $\nu(\text{Mo}=\text{O})$ and $\nu(\text{Mo}=\text{S})$ vibrations are rather strong and can readily be identified by intense bands. $\nu(\text{Mo}=\text{O})$ generally falls in the region of $800\text{--}1000\text{ cm}^{-1}$, depending upon the oxidation state and geometry of Mo [62]. When the metal is in a higher oxidation state the absorption occurs at a lower wavenumber and vice versa. Similarly $\nu(\text{Mo}=\text{S})$ falls in the region $480\text{--}550\text{ cm}^{-1}$ [60]. However, the situation becomes complicated when in addition to terminal sulfur if the compound contains $(\text{S}_2)^{2-}$ ligand; for $\nu(\text{S}_2)^{2-}$ vibration too is a strong one and normally appears in the region $480\text{--}600\text{ cm}^{-1}$ [63]. The situation could become more complicated if the compound under study is a tetraphenylphosphonium salt as $(\text{PPh}_4)^+$ vibration is a very strong one and masks the region $500\text{--}550\text{ cm}^{-1}$. Distinction between the $\nu(\text{Mo}=\text{S})$ and $\nu(\text{S}=\text{S})$ modes of vibrations can be made readily if the oxo analog of the

sulfido complex can be synthesized. In the case of oxo analog the region $480\text{--}600\text{ cm}^{-1}$ should show the presence of only $\nu(\text{S-S})$ vibration. A comparison of this mode of vibration with that of the corresponding sulfur analog of the compound can thus help to resolve the two vibrations related to $\nu(\text{S-S})$ and $\nu(\text{Mo=S})$ in this type of compounds.

The infrared spectra of the complexes synthesized are reproduced in Figs 4.1.1 to 4.1.9 and the absorption frequencies of some important vibrations are tabulated in Tables 4.1 to 4.4.

The identification and characterization of the complex $(\text{Et}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]$ poses no problem as the $(\text{Me}_4\text{N})^+$ salt is well known [51, 52]. The $\nu(\text{M=O})$ vibration appears at 950 cm^{-1} as an intense peak. The peak at 516 cm^{-1} is assigned to $\nu(\text{S-S})$ and the one at 467 cm^{-1} to $\nu(\text{Mo-S})$ bridging vibration. It has generally been observed that with the exception of $\nu(\text{Mo=O})$, the infrared spectra of the complexes, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ are very similar [24]. But in the case of $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$, the peak at 518 cm^{-1} shows splitting (Fig. 4.1.1). Since $\nu(\text{S-S})$ and $\nu(\text{Mo=S})$ are expected in this region, the splitting is a clear indication of the existence of both (Mo=S) and (S-S) bonds.

The pentavalent dimeric complexes $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ and $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ [80] have bands at 960 cm^{-1} assigned to $\nu(\text{Mo=O})$ stretching vibration (Fig. 4.1.2). In the case of the dioxo complex the peak splits into a doublet at 970 cm^{-1} and



A $(\text{Et}_4\text{N})_2 [\text{Mo}_2(\text{O})_2(\mu\text{-S})_2(\text{S}_2)_2]$

B $(\text{Et}_4\text{N})_2 [\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]$

C $(\text{nBu}_4\text{N})_2 [\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]$

FIG. 4.1.1 INFRARED SPECTRA.

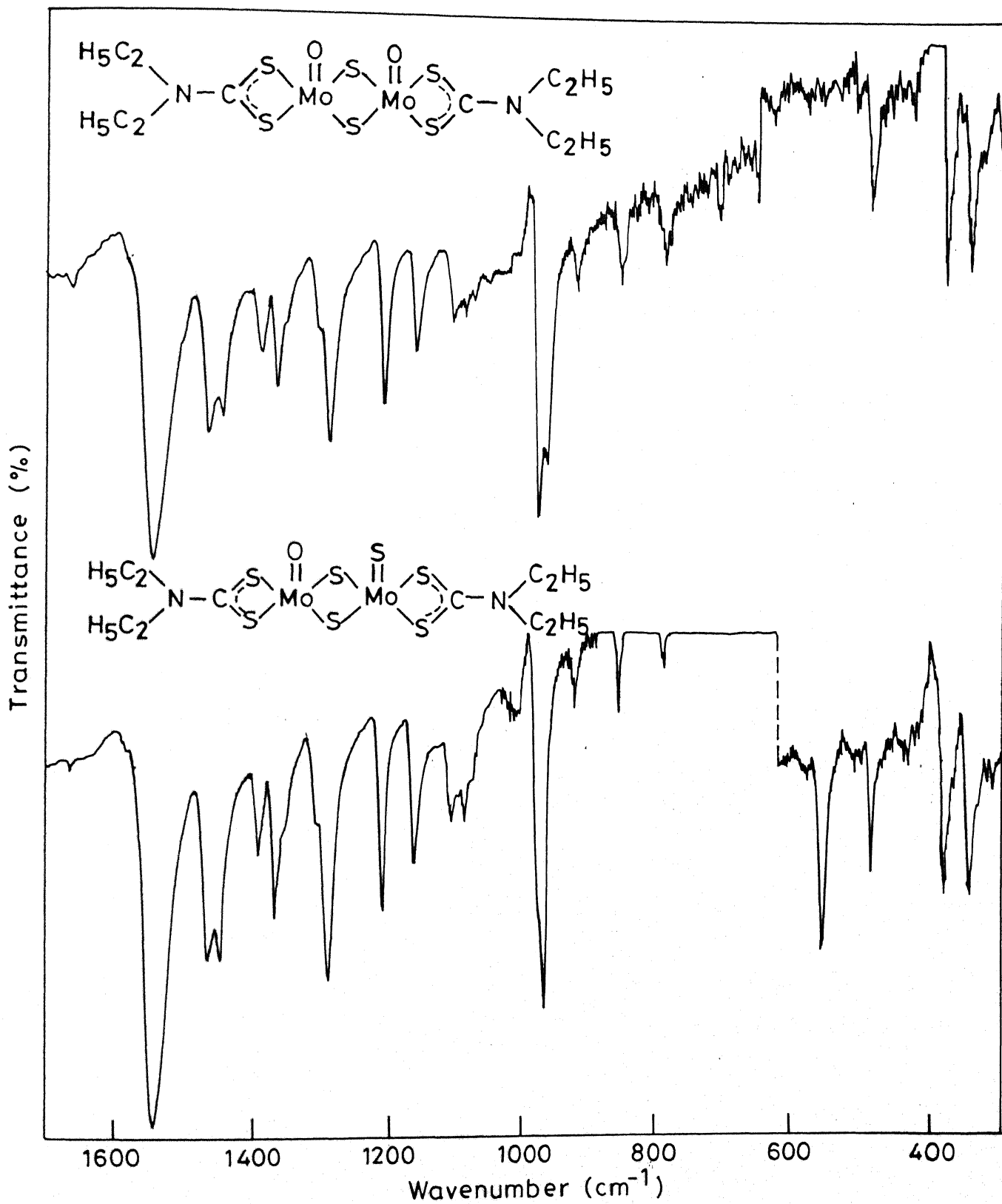


FIG. 4.1.2 INFRARED SPECTRA

960 cm^{-1} showing cis arrangement of Mo=O in $\{\text{Mo}_2(\mu\text{-S})_2\text{O}_2\}$ moiety. The peak at 550 cm^{-1} in the oxo-sulfido complex has been assigned to $\nu(\text{Mo}=\text{S})$. The vibrations at 480 and 350 cm^{-1} are due to the di μ -sulfido bridge [82]. All these assignments are consistent with that of the literature report [80]. $[\text{MoO}(\text{S}_2\text{CNET}_2)_2(\text{S}_2)]$ has the $\nu(\text{Mo}=\text{O})$ stretching vibrations at 910 and 920 cm^{-1} where the peak is split (Fig. 4.1.3). The $\nu(\text{S}-\text{S})$ vibration appears at 560 cm^{-1} and the spectrum is consistent with the literature reports [82]. The pentavalent monomeric compound $[\text{MoO}(\text{S}_2\text{CNET}_2)_2\text{Cl}]$ shows a strong absorption at 960 cm^{-1} characteristic of $\nu(\text{Mo}=\text{O})$ vibration. The other significant band at 1530 cm^{-1} is characteristic of the $\nu(\text{C}-\text{N})$ vibration of the dithiocarbamate (dtc) ligand (Fig. 4.1.3). When dtc acts as a bidentate ligand, this stretching frequency appears above 1500 cm^{-1} [84]. All these data are summarized in Table 4.1.

The infrared spectra of the dimeric complexes of the general formula $[\text{M}_2\text{L}_2\text{S}_9]^{2-}$ ($\text{M} = \text{Mo}, \text{W}; \text{L} = \text{O}, \text{S}$) are presented in Figs. 4.1.4 - 4.1.6. For, $[\text{Mo}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ the task of assignment is complicated as $\nu(\text{Mo}=\text{S})$ and $\nu(\text{S}-\text{S})$ vibrations overlap. The $(\text{Et}_2\text{NH}_2)^+$ salt shows absorption (Fig 4.1.4) at 522 cm^{-1} with shoulder at 527 cm^{-1} . Since in the oxo analog $\nu(\text{S}-\text{S})$ absorption appears around 530 cm^{-1} , the shoulder at 527 cm^{-1} may be assigned to $\nu(\text{S}-\text{S})$ and the band at 522 cm^{-1} to $\nu(\text{Mo}=\text{S})$. The $(\text{PPh}_4)^+$ salt shows a very intense peak at 525 cm^{-1} which masks the $\nu(\text{Mo}=\text{S})$ and $\nu(\text{S}-\text{S})$ vibrations. But the corresponding $(\text{AsPh}_4)^+$ salt shows clear cut peaks at 520 and 530 cm^{-1} assignable to $\nu(\text{Mo}=\text{S})$ and

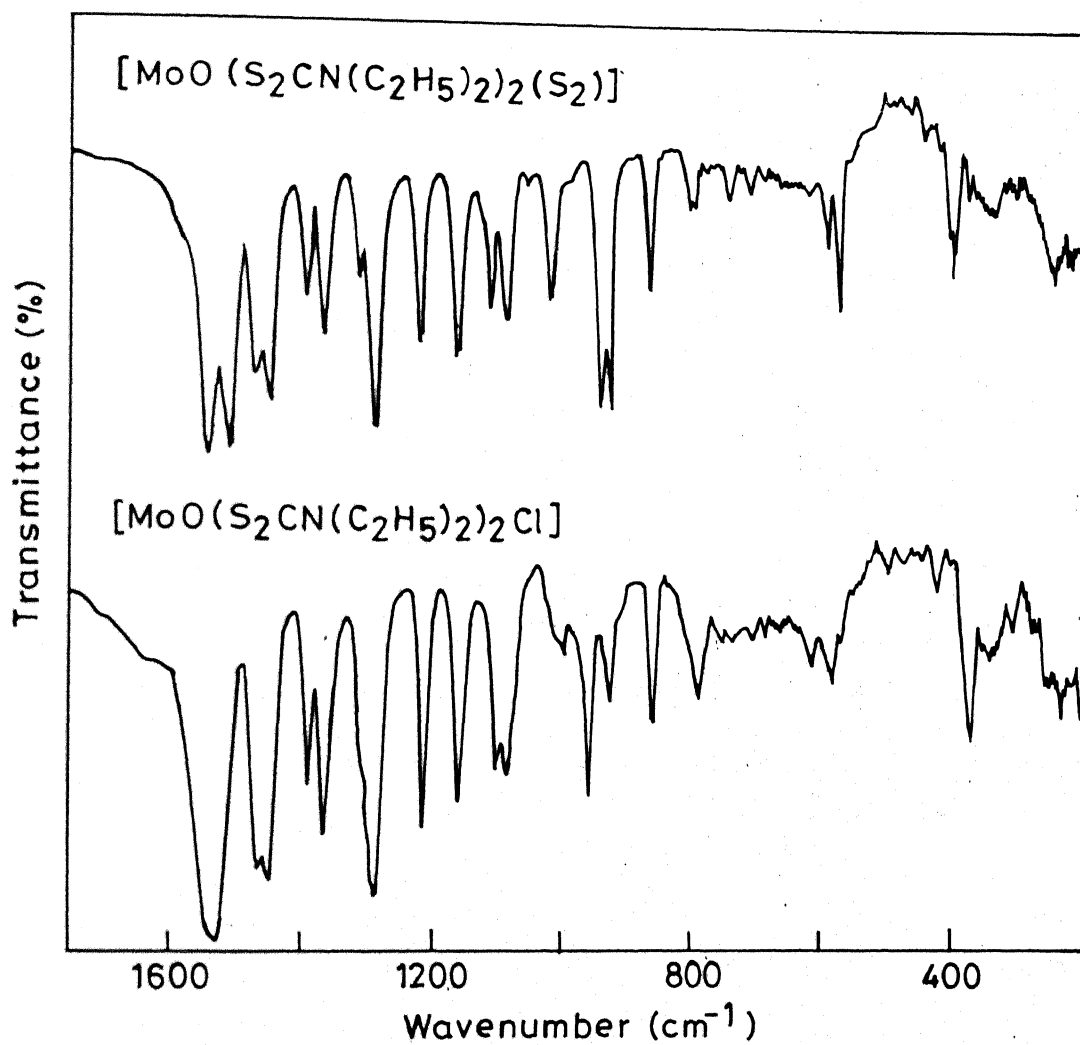


FIG. 4.1.3 INFRARED SPECTRA.

Table 4.1 Infrared Spectral Data of [Mo - S] complexes in cm^{-1}

Compound	$\nu(\text{M}=\text{O}_t)$	$\nu(\text{S}-\text{S})$	$\nu(\text{M}-\text{S}_t)$	$\nu(\text{M}-\text{S}_b)$	Other Important vibrations	Ref
$(\text{Et}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2)_2]$	925(s)	516(m)	---	467(m)	357(w), 321(w) (Mo-S ₂)	This work
$(\text{Et}_4\text{N})_2[\text{Mo}_2\text{OS}(\mu-\text{S})_2(\text{S}_2)_2]$	940(s)	---	518(s)	460(m) 350(m)	~800 (Et_4N^+)	-do-
$(\text{Et}_4\text{N})_2[\text{Mo}_2\text{S}_2(\mu-\text{S})_2(\text{S}_2)_2]$	---	520	535	460 350	---	14
$[\text{Mo}_2\text{O}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$	970 960	---	---	480(m) 380(m) 345(m)	1545(s) (C-N)	This work
$[\text{Mo}_2\text{OS}(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$	965(s)	---	550	485(m) 380(m) 345(m)	1545(s) (C-N)	80
$[\text{Mo}_2\text{S}_2(\mu-\text{S})_2(\text{S}_2\text{CNET}_2)_2]$	---	---	548(m) 538(sh)	463 334	---	80
$[\text{MoO}(\text{S}_2\text{CNET}_2)_2(\text{S}_2)]$	920(s)	560(m)	---	---	1540(s) (C-N)	This work
$[\text{MoO}(\text{S}_2\text{CNET}_2)_2\text{Cl}]$	960(s)	---	---	---	1530(s) (C-N)	-do-

s = strong; m = medium; w = weak; t = terminal; b = bridging

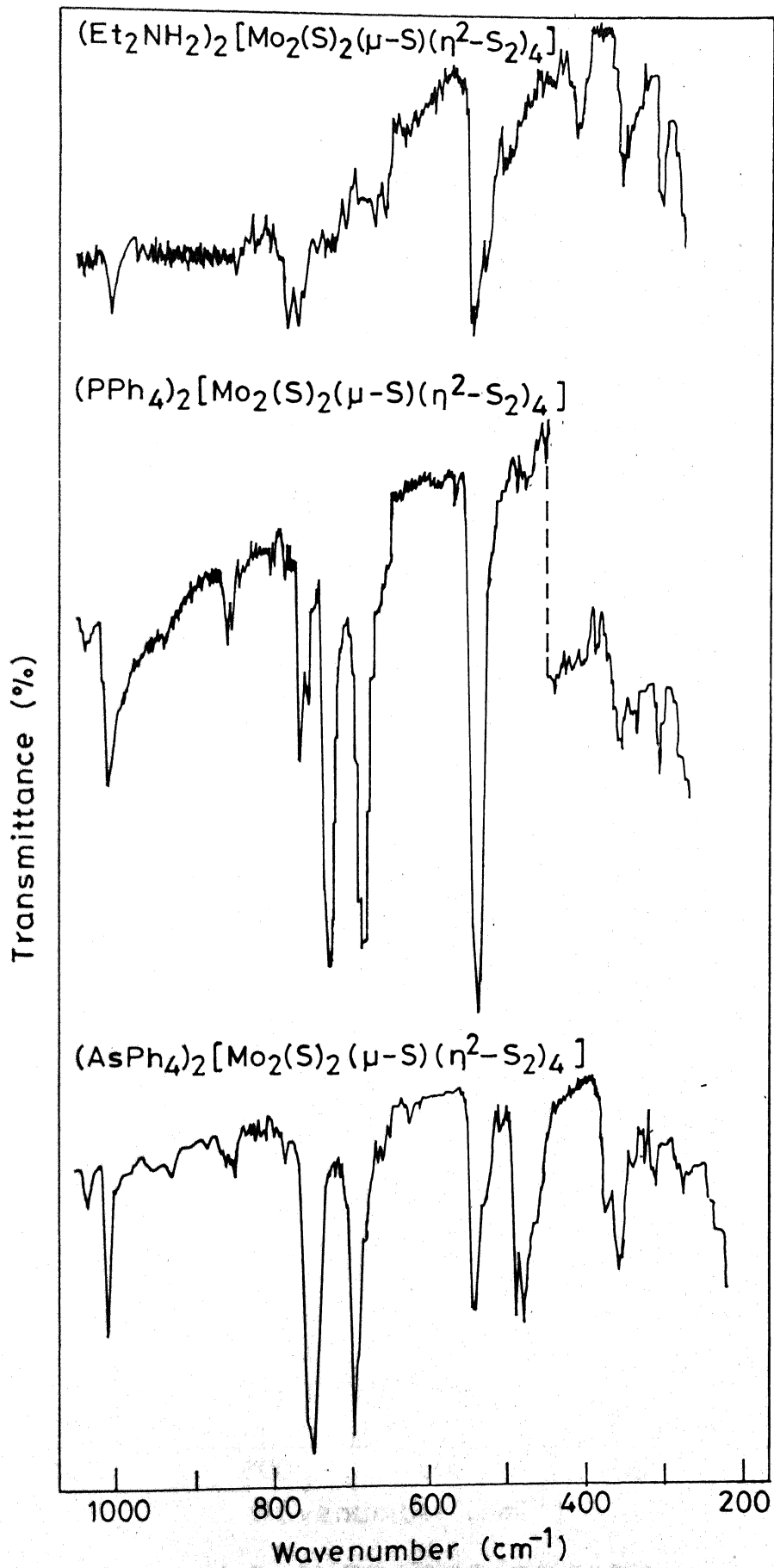


FIG. 4.1.4 INFRARED SPECTRA

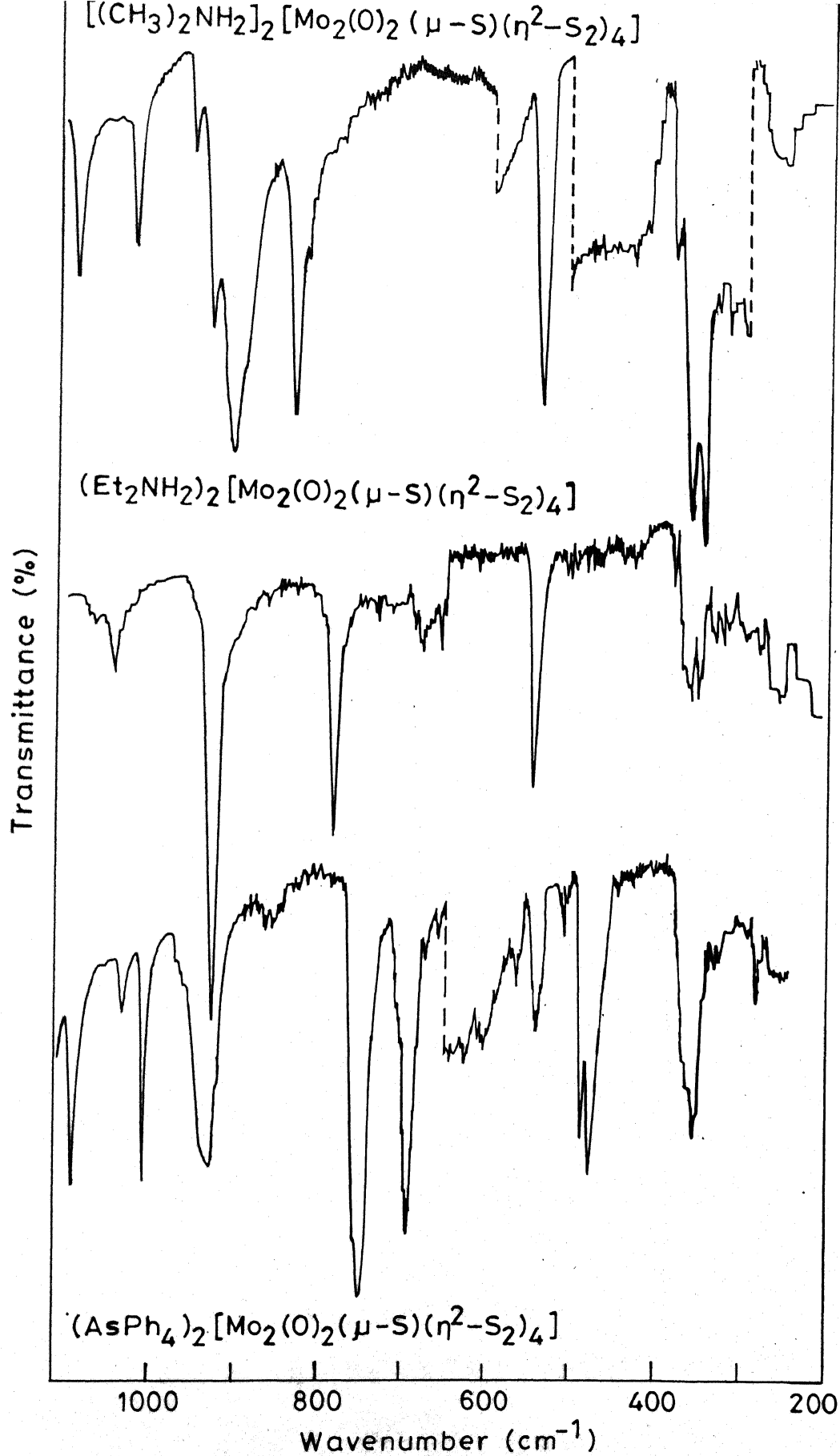


FIG. 4.1.5 INFRARED SPECTRA.

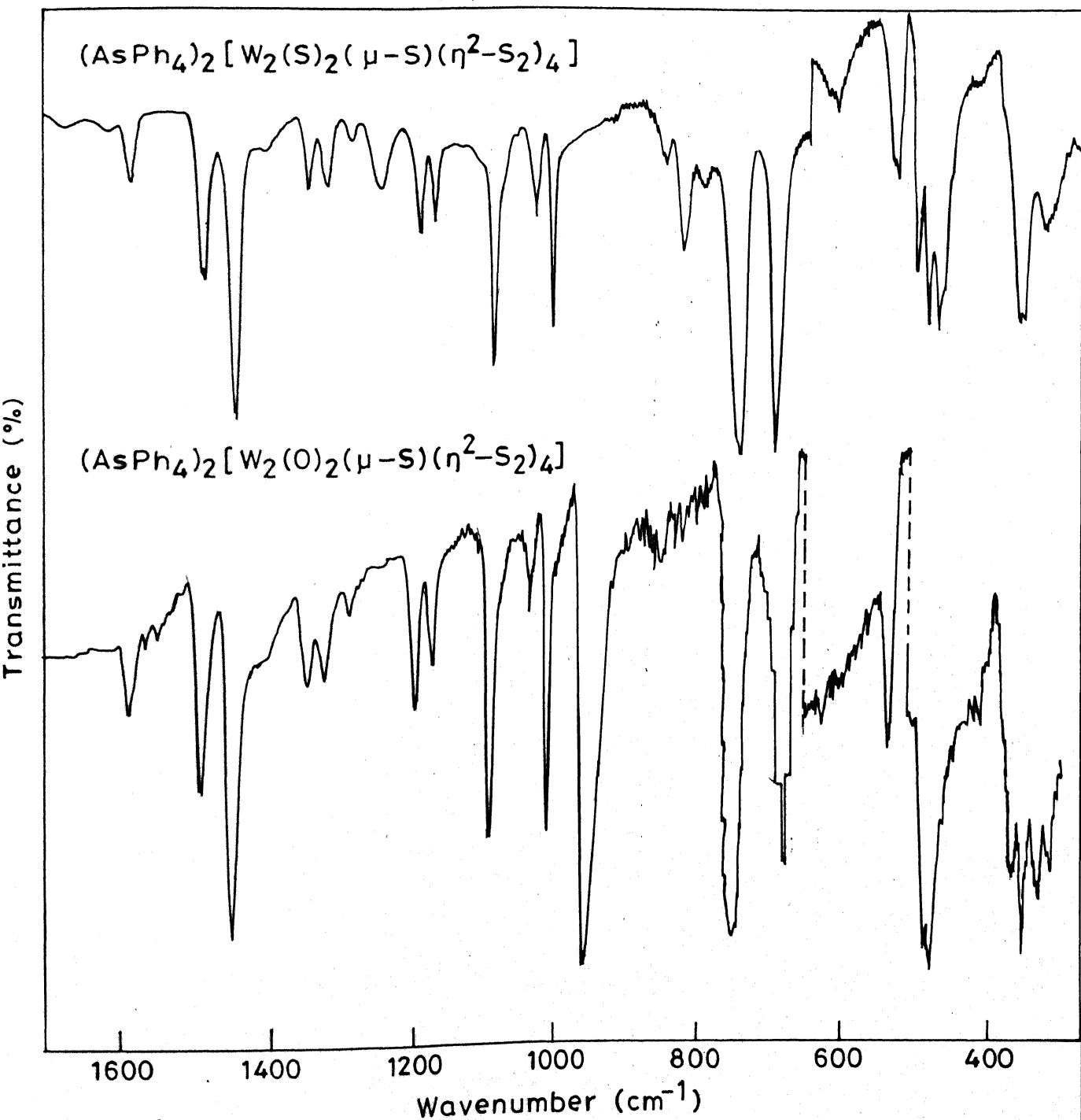


FIG. 4.1.6 INFRARED SPECTRA.

(S-S) respectively. The tungsten analog shows vibrations at 525 cm^{-1} and 495 cm^{-1} which are assigned to $\nu(\text{S-S})$ and $\nu(\text{W-S})$ respectively. Since $\nu(\text{S-S})$ vibration remains unaffected in the Mo or W compounds, it is easy to assign the 525 cm^{-1} band to $\nu(\text{S-S})$ which then leaves only the strong band at 495 cm^{-1} assignable to $\nu(\text{W=O})$ and this is in good agreement with the data reported earlier [25]

The dimeric complex, $[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ shows a strong absorption around 925 cm^{-1} (Fig. 4.1.5). The $[(\text{CH}_3)_2\text{NH}_2]^+$ salt has absorption at 910 cm^{-1} whereas the $(\text{Et}_2\text{NH}_2)^+$, $(\text{AsPh}_4)^+$ and $(\text{Et}_4\text{N})^+$ [84] salts all show absorption at 920-926 cm^{-1} . The $(\text{Me}_4\text{N})^+$ salt shows a doublet at 950 and 920 cm^{-1} [85]. In the tungsten analog $\nu(\text{W=O})$ appears around 940 cm^{-1} [86], which is slightly higher than $\nu(\text{Mo=O})$ observed in the molybdenum analogs, though tungsten is heavier. This suggests the involvement of stronger multiple bonding between tungsten and oxygen compared to molybdenum and oxygen. In both molybdenum and tungsten oxo complexes, the band around 530 cm^{-1} is assigned to $\nu(\text{S-S})$ vibrations which is comparable with the values for disulfido complexes reported in the literature [63].

When $(\text{S}_2)^{2-}$ coordinates in a side-on fashion, the local symmetry of the $\{\text{M}(\text{S})\}$ moiety is C_{2v} , for which the expected normal mode of vibrations are $\nu(\text{S-S})$, (A_1) , $\nu(\text{M-S})$ (A_1) of $\{\text{M}(\text{S})\}$ moiety and $\nu_{\text{as}}(\text{M-S})$ (B_1) respectively [64, 87]. All these vibrations are IR active. The exact identification of the ν_{S} and ν_{as} vibrations are difficult because of the possible coupling of the

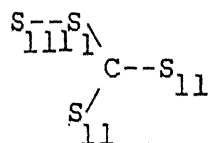
Table 4.2. Infrared Spectral Data of Dimeric [M(VI)-S] Complexes in cm^{-1}

Compound	$\nu(\text{M=O})$	$\nu(\text{M=S})$	$\nu(\text{S-S})$	$\nu(\text{M-S})$	Other important vibrations	Ref
$(\text{Et}_4\text{N})_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	926	---	528	---	---	84
$((\text{CH}_3)_4\text{N})_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	950, 920	---	530	360, 342	---	85
$(\text{AsPh}_4)_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	920(s)	---	535(m)	350(m)	480(s), 490(sh) $(\text{AsPh}_4)^+$; 700(s), 750(sh) (C-H)	This work
$(\text{Et}_2\text{NH}_2)_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	925(s)	---	535(m)	360, 340(m)	790(m) (C-H)	-do-
$((\text{CH}_3)_2\text{NH}_2)_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	910(s)	---	535(m)	360, 340(m)	840(m) (C-H)	-do-
$(\text{AsPh}_4)_2[\text{Mo}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	---	520(s)	530(m)	350(m)	480(s), 490(sh) $(\text{AsPh}_4)^+$; 700(m), 750(m) (C-H)	-do-
$(\text{Et}_2\text{NH}_2)_2[\text{Mo}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	---	522(s)	527(m)	360(m)	770(m), 790(m) (C-H)	-do-
$(\text{PPh}_4)_2[\text{W}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	---	492(s)	---	345(w), 320(m) 302(w)	527(vs) $(\text{PPh}_4)^+$	25
$(\text{AsPh}_4)_2[\text{W}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	---	495(s)	525(m)	360(m)	470(s), 485(sh) $(\text{AsPh}_4)^+$	This work
$(\text{PPh}_4)_2[\text{W}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	938(s)	---	---	348(w), 326(w) 311(w)	---	86
$(\text{AsPh}_4)_2[\text{W}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	945(s)	---	527(m)	355(w), 347(m) 325(w)	470(s), 485(sh) $(\text{AsPh}_4)^+$ 700(s), 750(s) (C-H)	This work
$[\text{MoO}(\text{S}_2\text{CNEt}_2)_2(\text{S}_2)]$	920(s)	---	560(m)	---	1540(s) (C-N)	-do-

M = Mo, W ; vs = very strong; s = strong; m = medium; w = weak; sh = shoulder

A_1 mode with that of $\nu(S-S)$. The vibrations in the lower region, around 350 cm^{-1} can be assigned to ν_s and ν_{as} . The singly bridged $\nu\{M-S-M\}$ vibrations in these complexes are very weak in nature and hence the assignment for this vibration is difficult. The infrared data of the hexavalent dimeric complexes are listed in Table 4.2.

The infrared spectra of the complexes containing coordinated thiocarbonate and perthiocarbonate ligands are reproduced in Figs. 4.1.7 and 4.1.8 and the important band positions are listed in Table 4.3. The perthiocarbonate ligand has a non-tetrahedral structure as shown below.



and the planarity of this ion has been established using Hückel MO method [88]. Hence the delocalization of the π -electron density could be anticipated when this ligand is chelated to a metal center. The infrared spectrum of the ammonium salt of this ion shows four bands of medium intensity each at 955, 825, 510 and 485 cm^{-1} [88]. The bands at 955 and 835 cm^{-1} are assigned to A_1 and B_1 vibrations which arise from ν_3 (E') vibration of trithiocarbonate ion by reducing its symmetry (C_{2v}). These are not pure stretching vibrations but a mixture of both $\nu(C=S_1)$ and $\nu(C=S_{11})$ vibrations. The bands at 519 and 485 cm^{-1} are assigned to a symmetric vibration (A_1) of the whole $CS_1(S_{11})_2$ group and for a deformation vibration of B_2 mode. It is difficult to pinpoint which of the vibrations arise from A_1 and which one from B_1 mode.

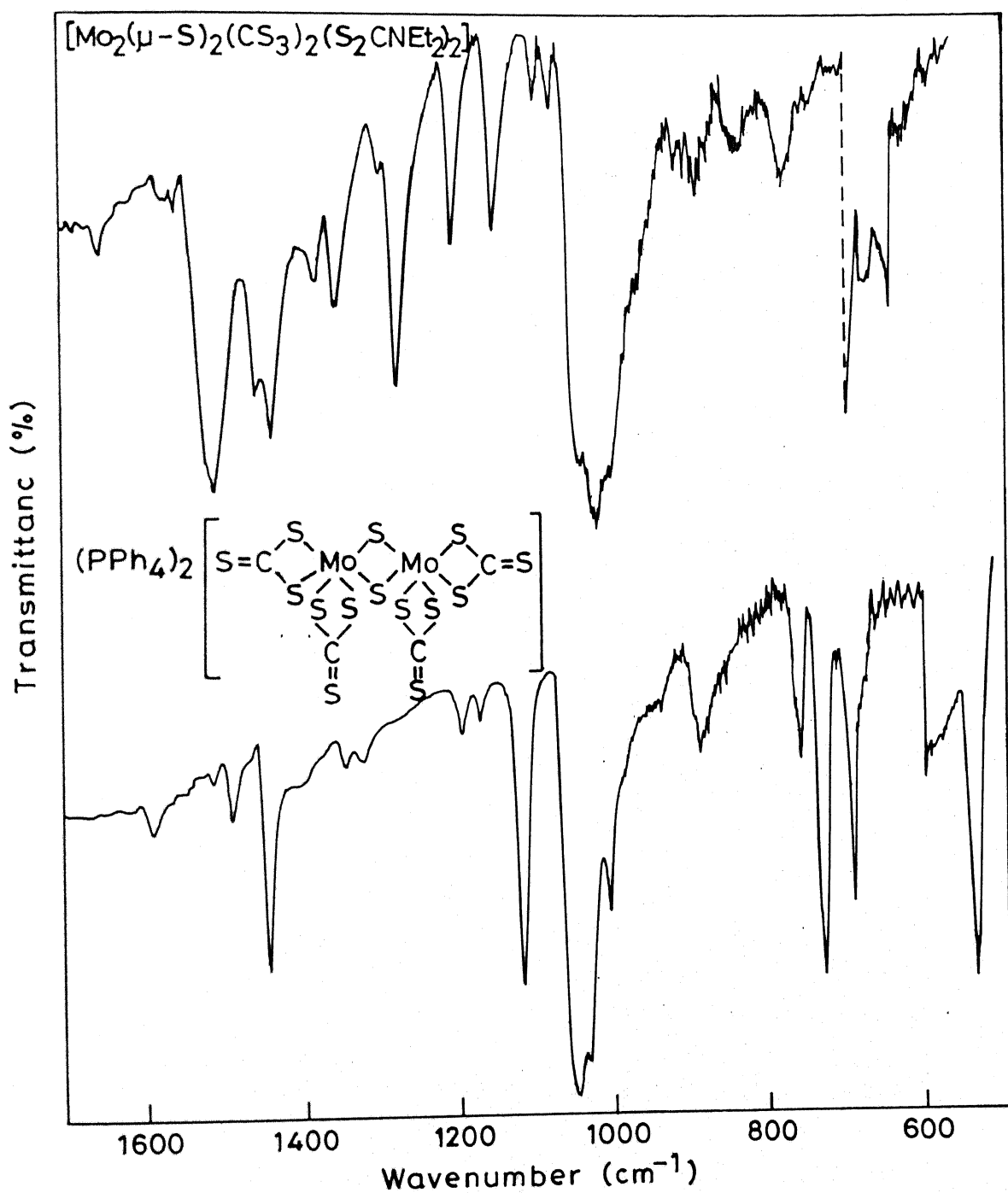


FIG. 4.1.8 INFRARED SPECTRA.

Table 4.3 Infrared Spectral Data of Perthiocarbanato complexes in cm^{-1}

Compound	$\nu(\text{C}=\text{S})$	$\nu(\text{Mo}-\text{S}-\text{Mo})$	$\nu(\text{Mo}=\text{O})$	Other important vibrations	Ref
$(\text{PPh}_4)_2[\text{MoS}(\text{CS}_4)_2] \cdot \text{DMF}$	$\sim 980(\text{s})$	---	---	---	73
$(\text{PPh}_4)_2[(\text{CS}_4)(\text{CS}_3)\text{MoO}]$	990(s) 1010(sh)	---	930(s)	527 $(\text{PPh}_4)^+$; 690, 730, 770 (C-H)	This work
$(\text{PPh}_4)_2[\text{Mo}(\mu-\text{S})_2(\text{CS}_3)_4]$	1050(s) 1040(sh) 1000(sh)	450(w)	---	527 $(\text{PPh}_4)^+$; 690, 730, 770 (C-H)	-do-
$[\text{Mo}_2(\mu-\text{S})_2(\text{CS}_3)_2(\text{S}_2\text{CNEt}_2)_2]$	1020(s) 1015(sh)	450(w)	---	1510 (C-N)	-do-
$(\text{PPh}_4)_2[\text{Ni}(\text{CS}_4)_2]$	1030(s) 965, 910 850	---	---	---	93

s = strong; m = medium; w = weak

Moreover, when $(CS_4)^{2-}$ is coordinated as bidentate ligand the infrared spectrum is more complicated and as most of the vibrations can mix with one another, no meaningful analysis can be made. But for characterization purpose one can still identify $\nu(C=S)$ vibration as one of the free $(C=S_{11})$ of the coordinated ligand. In the literature, for the $(CS_4)^{2-}$ ligand coordinated to Mo, a strong infrared absorption at 980 cm^{-1} has been attributed to the $\nu C=S$ asymmetric stretching vibration [73]. The complex $(PPh_4)_2[MoO(CS_3)(CS_4)]$ shows a strong absorption band at 990 cm^{-1} with a sharp shoulder at 1010 cm^{-1} . The 990 cm^{-1} band could be assigned to C=S asymmetric stretch of $(CS_4)^{2-}$, in line with the earlier report [73], while the shoulder could be attributed to exo-cyclic stretching mode $\nu(C=S)$ of CS_3^{2-} in accordance with the assignment of Burke and Fackler [89]. Two other compounds with coordinated $(CS_3)^{2-}$ ligands, $[Mo_2(\mu-S)_2(CS_3)_2(S_2CNet_2)_2]$ and $(PPh_4)_2[Mo(\mu-S)_2(CS_3)_4]$, show the asymmetric stretching vibration of C=S of the CS_3 group around 1020 cm^{-1} [90].

In the dithiolene complexes the C=C stretching frequency is a rough measure of the C=C bond strength as it couples very little with the other modes of vibrations. The $\nu C=C$ stretching frequency would be mainly dependent on the substituent group on the acetylenic carbon atoms. When $R = (COC_6H_5)$ the C=C stretching frequency is found to be about 60 cm^{-1} less than when $R = (COOCH_3)$. A lower value of the $\nu(C=C)$ vibration in the $-(COC_6H_5)$ substituted complex indicates a better π -electron delocalization than in the $-(COOCH_3)$ substituted dithiolene complex [91]. For

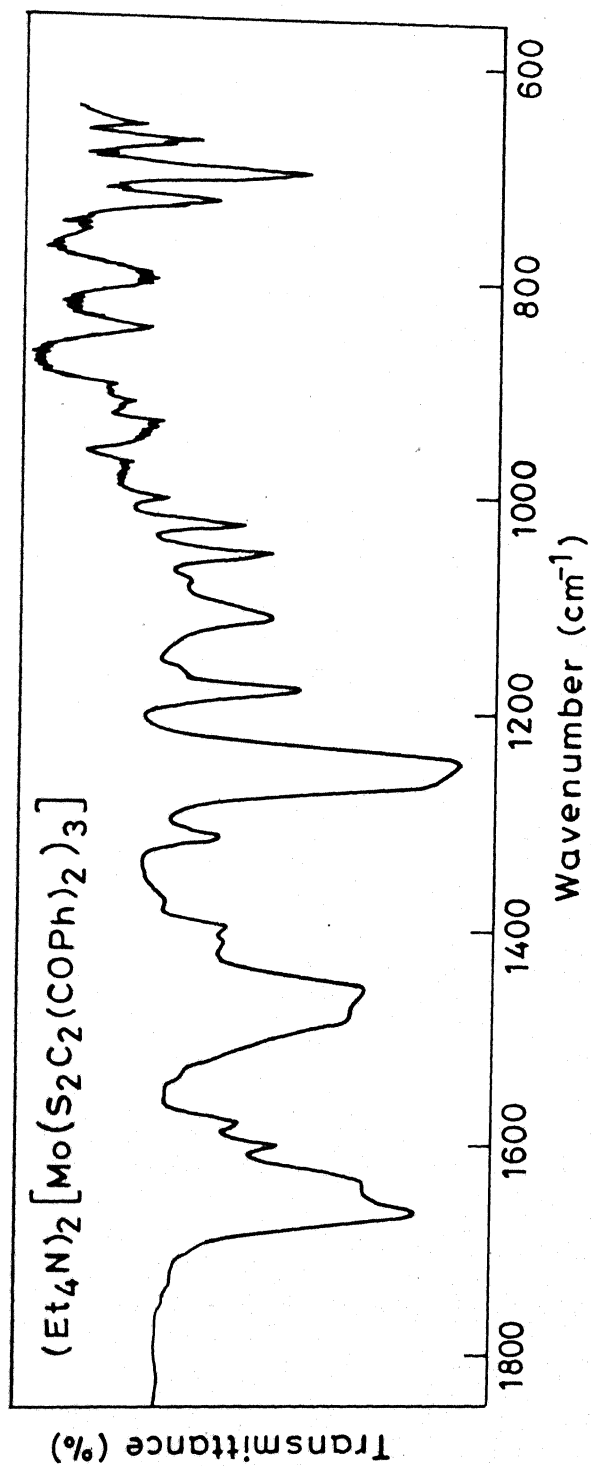


FIG. 4.1.9 INFRARED SPECTRA.

Table 4.4 Infrared Spectral Data of Monomeric [Mo(IV)-S]
Complexes in cm^{-1}

Compound	$\nu(\text{Mo}=\text{O})$	Other important vibrations	Ref
$(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$	860(s)	480(w) (Mo-S)	45, This work
$(\text{Et}_4\text{N})_2[\text{MoO}(\text{S}_4)_2]$	930(s)	420(w), 375(w), 335(w) (Mo-S ₄)	-do-
$(\text{Et}_4\text{N})_2[\text{MoO}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]$	950(s)	1660(s) (C=O); 1490(m) (C=C)	-do-
$(\text{Et}_4\text{N})_2[\text{Mo}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	---	1660(s) (C=O); 1470(m) (C=C)	This work
$(\text{PPh}_4)_2[\text{Mo}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3]$	---	1710, 1730 (C=S)	49
$(\text{Et}_4\text{N})_2[\text{W}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]$	---	1665(s) (C=O) 1445(s) (C=C)	48, 57

s = strong; m = medium; w = weak.

the compounds $[\text{MoO}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^{2-}$ and $[\text{Mo}(\text{S}_2\text{C}_2(\text{COPh})_2)_3]^{2-}$ (Fig. 4.1.9), the absorptions at ~ 1490 and 1660 cm^{-1} have been assigned to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ respectively which is in agreement with earlier work [92, 93]. The infrared spectral data of dithiolene complexes are listed in Table 4.4.

4.1.2 Electronic Spectra

The electronic spectra were recorded on Shimadzu UV-190 and Varian Cary 2200 double beam spectrophotometers using matched quartz cells. The solvents CH_3CN and DMF were distilled and stored over molecular sieves (4 Å) before use.

The electronic absorption spectra of the complexes synthesized are reproduced in Figs. 4.1.10 to 4.1.16. The absorption maxima for these complexes are tabulated in Table 4.5 and 4.6. For the dimeric compounds, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ the electronic spectral data are very much similar to the reported data, where a different synthetic strategy has been used [24, 52]. Similarly $[\text{MoO}(\text{S}_2\text{CNET}_2)_2(\text{S}_2)]$ has also been identified by electronic spectroscopy which is identical to the reported one [82]. For, $[\text{Mo}^{\text{V}}\text{O}(\text{S}_2\text{CNET}_2)_2\text{Cl}]$, the electronic spectrum shows band maxima at 520, 455, 442, 390 and 270 nm (Fig. 4.1.11). The band at 270 nm is assigned to the intraligand transitions [94], 442 and 390 nm to LMCT (Ligand to metal charge transfer) [64]. The low energy transition at 520 nm may be assigned to $^2\text{B}_2 \rightarrow ^2\text{E}$ and the band at 455 nm to $^2\text{B}_2 \rightarrow ^2\text{B}_1$ [95].

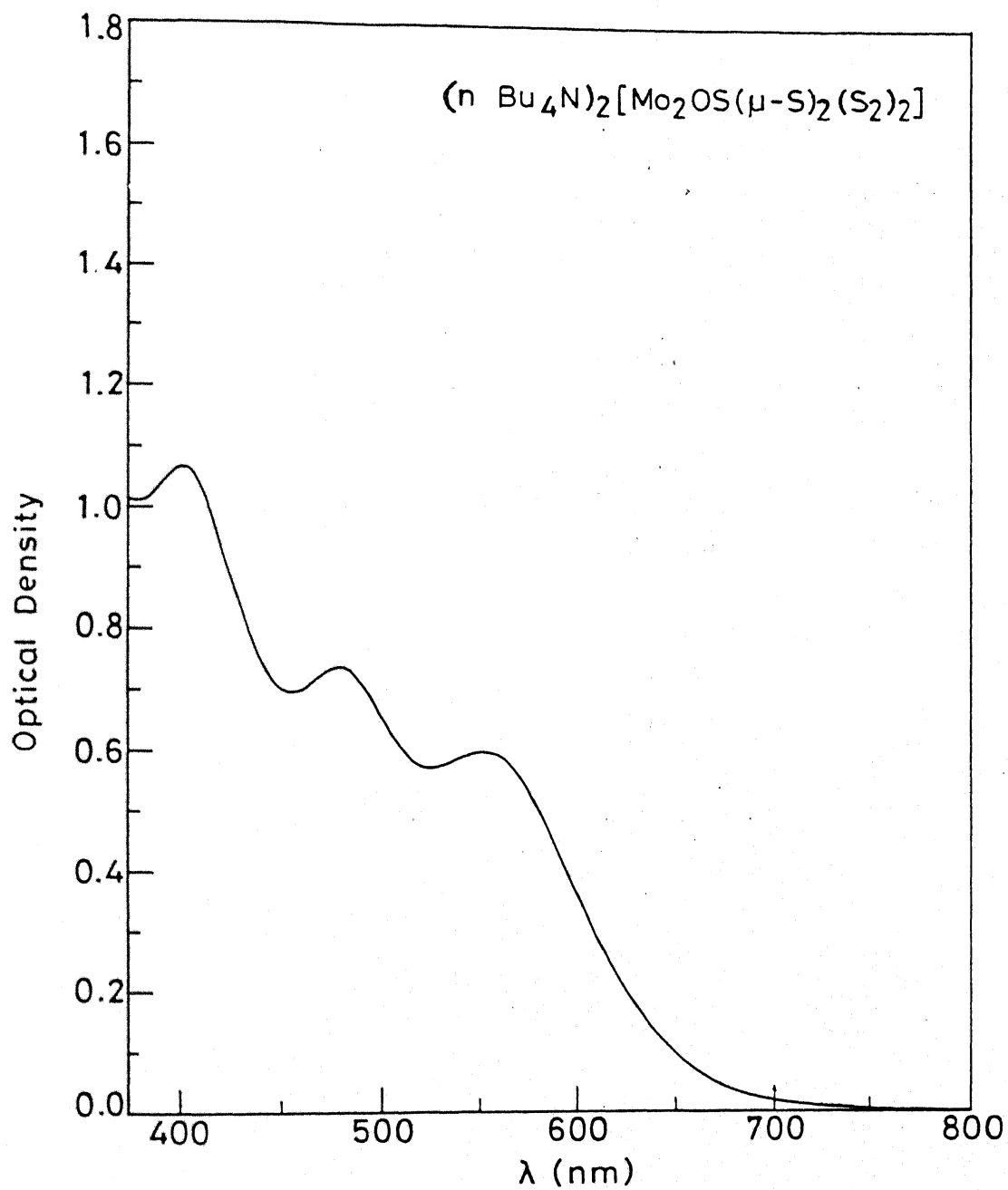


FIG. 4.1.10 ELECTRONIC SPECTRUM.

FIG. 4.1.11 ELECTRONIC SPECTRA

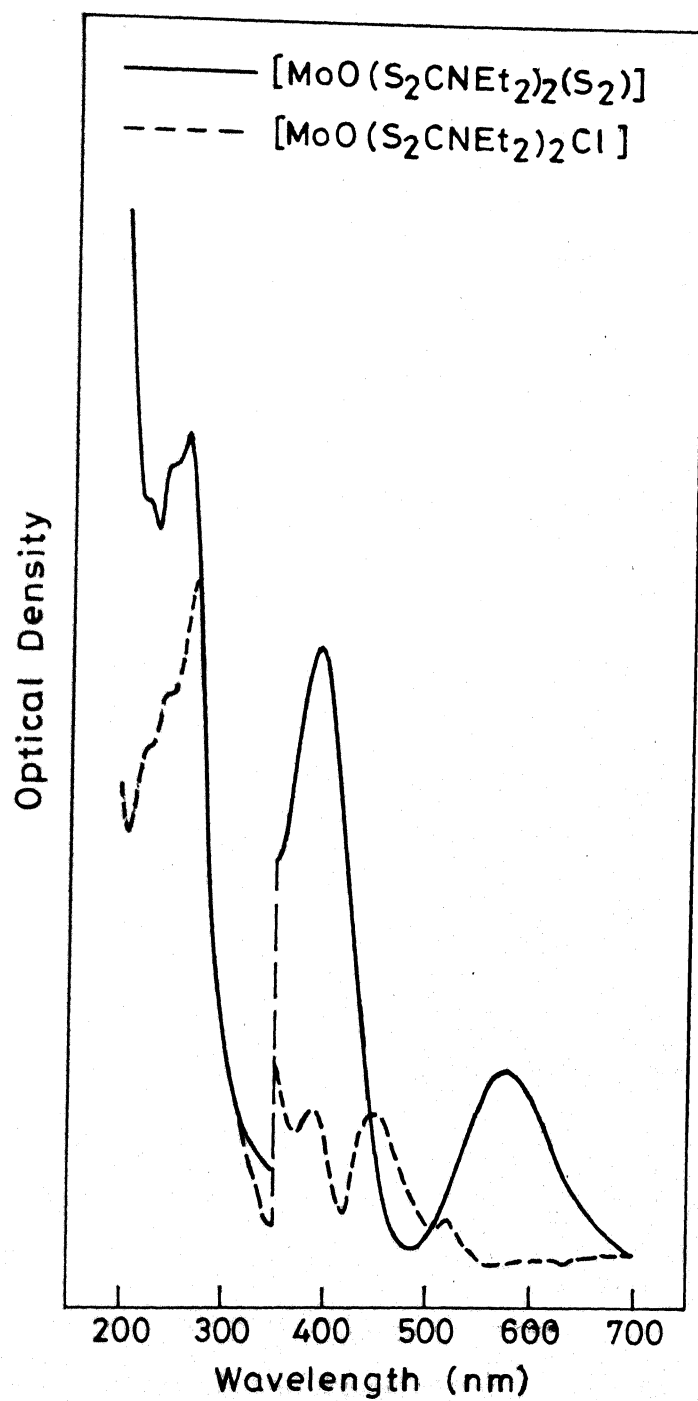


FIG. 4.1.11 ELECTRONIC SPECTRA

For $[\text{Mo}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$, the higher energy band at 400 nm may be assigned to $\pi_v \rightarrow d(\text{Mo})$ [63, 96, 97]. This is a LMCT transition which is influenced by the oxidation state, metal-metal bonding and the nature of the ligands which determine the energy of LUMO and its metal character. The lowest energy band at 590 nm is assigned to a charge transfer (CT) transition from $(\text{S}_2)^{2-}$ to (Mo-S_t) (t = terminal) antibonding orbital. The band at 485 nm then corresponds to a CT transition from bridging sulfur to (Mo-S_t) antibonding orbital [67]. The corresponding tungsten system $[\text{W}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ shows electronic spectrum similar in nature and thus the origin of these bands may be due to similar transitions. As expected all these absorption bands are shifted hypsochromically compared to the corresponding molybdenum analog (Table 4.6).

The oxo analogs, $[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ and $[\text{W}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ show electronic spectra which differ compared to the corresponding all sulfur analog. This suggests that the terminal oxo of the $\{\text{M}=\text{O}\}$ group ($\text{M} = \text{Mo}, \text{W}$) interact with the rest of the molecule differently compared to the $\{\text{M}=\text{S}\}$ group in these complexes. It has been shown by Bernholc and Stiefel that the HOMO-LUMO gap in the dimers, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$, differs considerably [67]. The replacement of oxygen atoms by S atoms in these systems significantly alter the energies and Mulliken's populations of the remaining low lying levels. This has been viewed due to the substantial delocalization of the

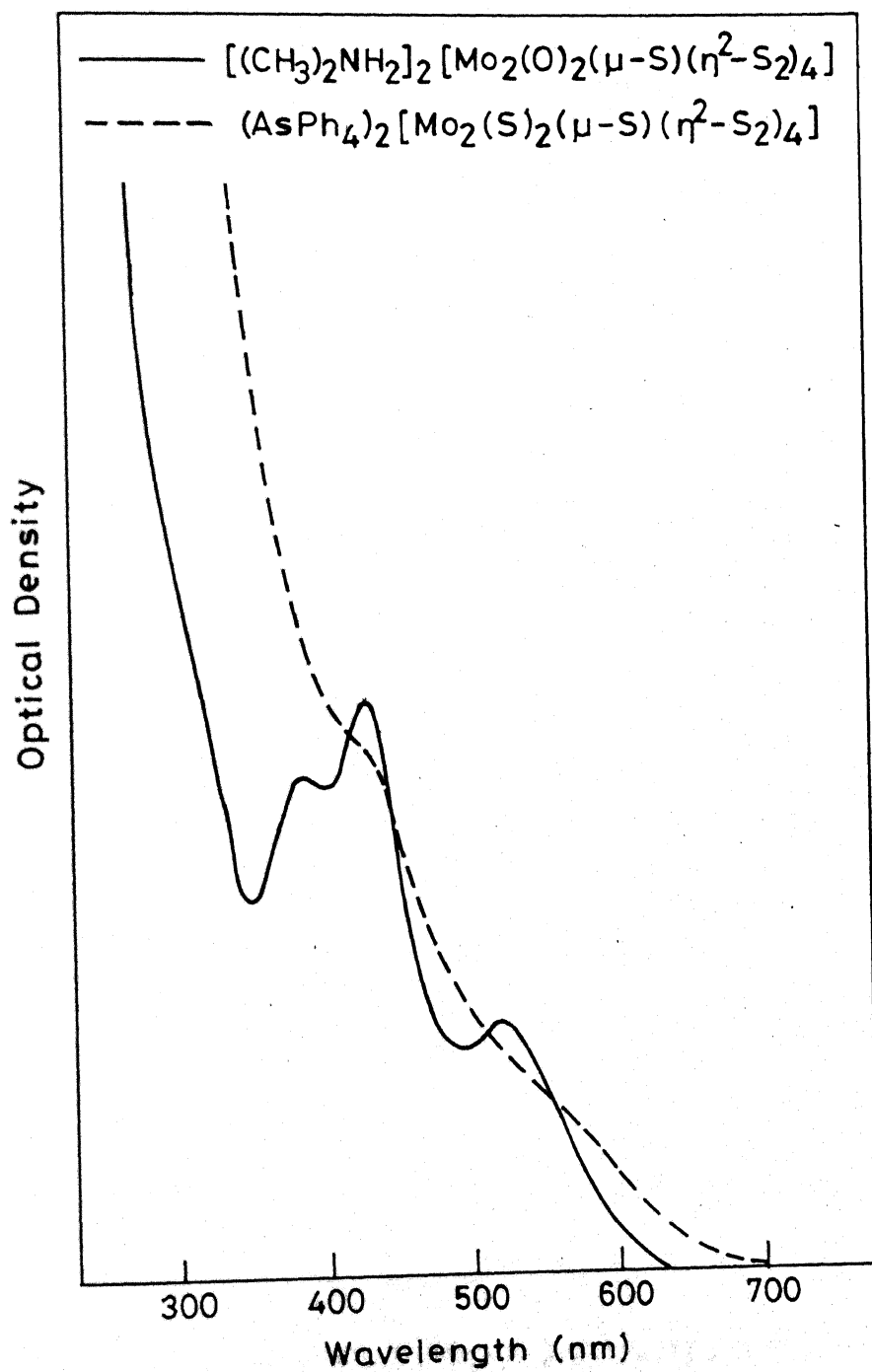


FIG. 4.1.12 ELECTRONIC SPECTRA

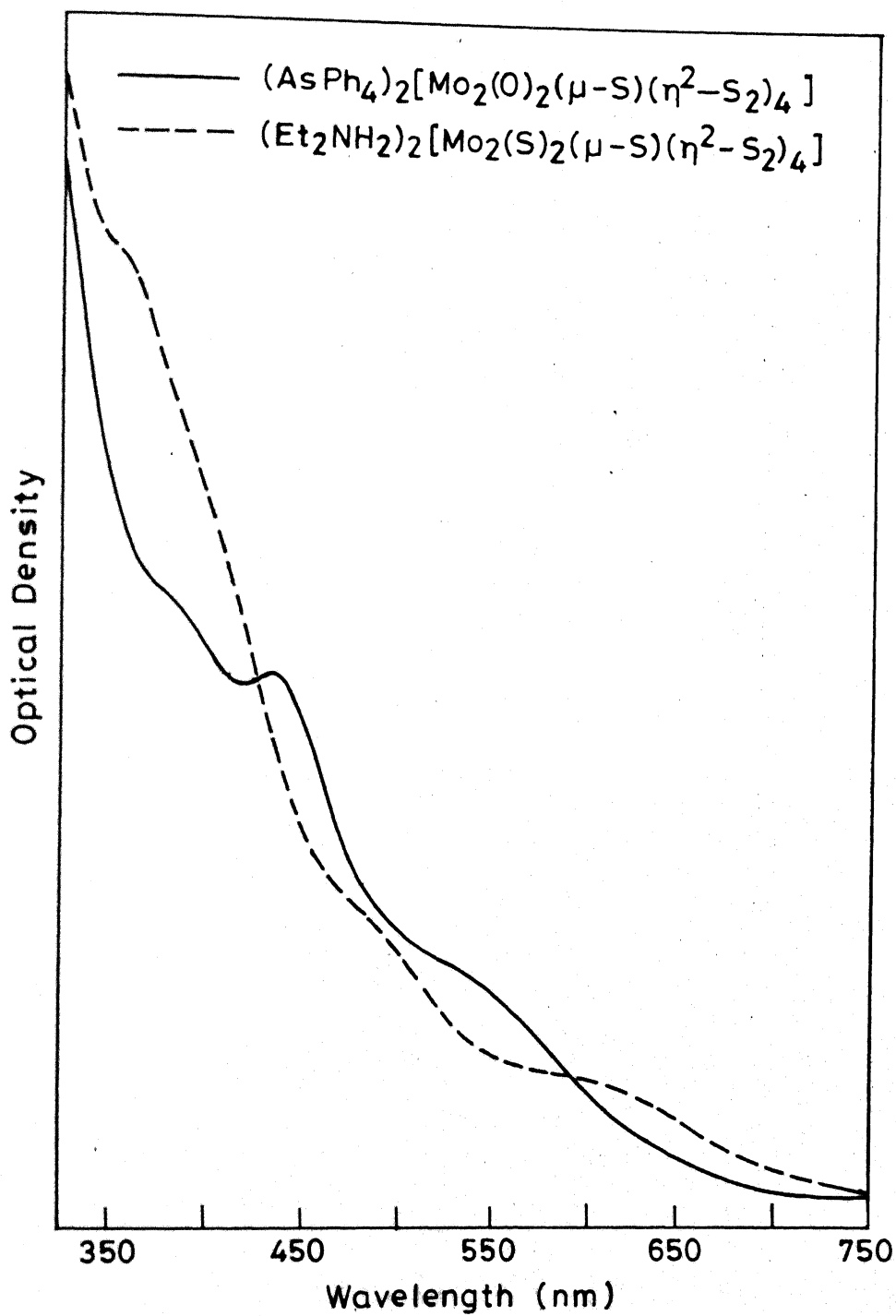


FIG. 4.1.13 ELECTRONIC SPECTRA

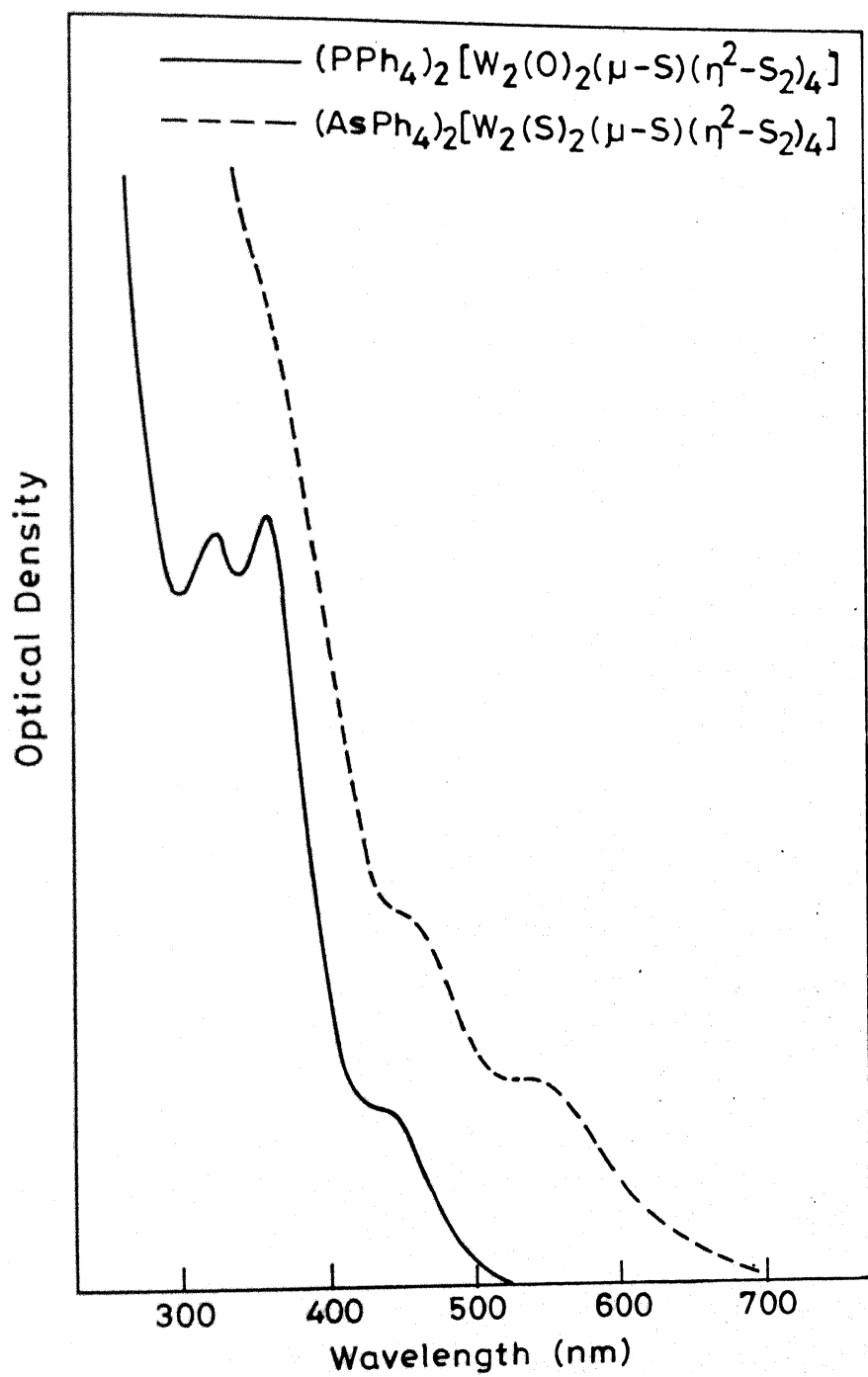


FIG. 4.1.14 ELECTRONIC SPECTRA.

molecular orbitals in $\{M=S\}$ systems [98, 99]. In the case of $\{M=O\}$ systems the restricted delocalization introduces small admixtures of $\{M=O\}$ orbitals into the other orbitals. However, much greater splitting between the $\{M=O\}$ bonding and antibonding states is observed compared to the corresponding $\{M=S\}$ splittings. In the light of these arguments the band observed around 520 nm in $[Mo_2O_2(\mu-S)(S_2)_4]^{2-}$ may be assigned to a CT transition from $(S_2)^{2-} \rightarrow \{Mo=O_t\}$ antibonding orbital. The band at 430 nm then corresponds to a CT band from $S_{br} \rightarrow \{Mo=O_t\}$ antibonding orbital. The highest energy band at 390 nm may be assigned to $\pi_v \rightarrow d(Mo)$. The three transitions observed for $[W_2O_2S_9]^{2-}$ can also be assigned similarly.

Extensive studies on the electronic spectra of the nickel dithiolene complexes have been carried out and the assignments of electronic bands for similar systems are available in the literature [92]. In the case of $[MoO(S_2C_2(COPh)_2)_2]^{2-}$, the band at 400 and 338 nm are assigned to LMCT and the band at 310 nm is attributed to intra-ligand charge transfer [45]. Dramatic changes have been observed in the band positions and intensity with the change of the substituents in $[S_2C_2R_2]^{2-}$, ($R = COPh, COOMe$) [93]. In the case of tris(dithiolene) complexes, $[Mo(S_2C_2(COPh)_2)_3]^{2-}$, when $R = COPh$, the compound absorbs at 587, 406 and 325 nm whereas when $R = COOMe$, the bands appear at 650, 450 and 356 [49]. In the tungsten complex, $[W(S_2C_2(COPh)_2)_3]^{2-}$, only two absorptions in the visible region, at 600 and 448 nm are observed as against three in the corresponding Mo systems. Stiefel et al have also

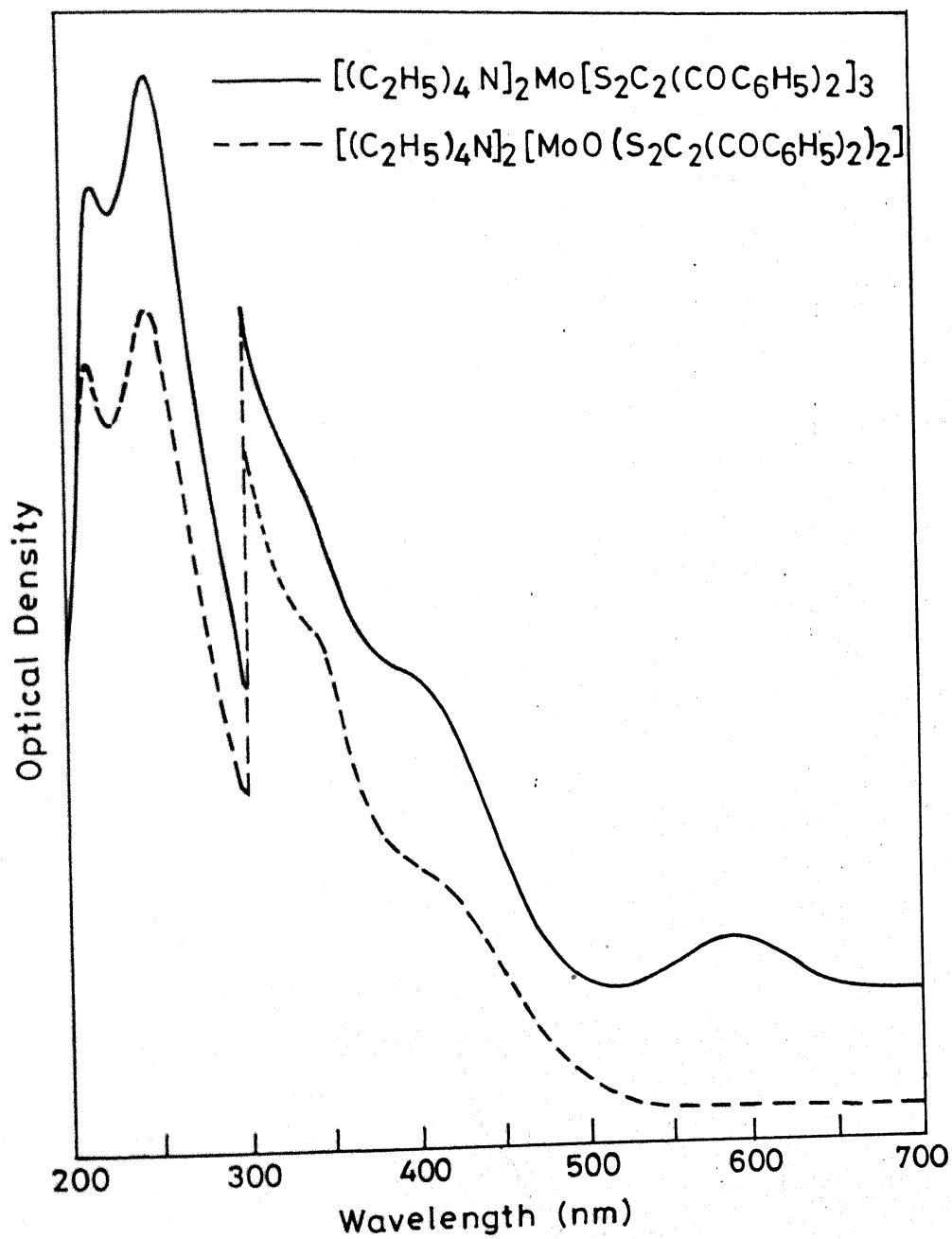


FIG. 4.1.15 ELECTRONIC SPECTRA.

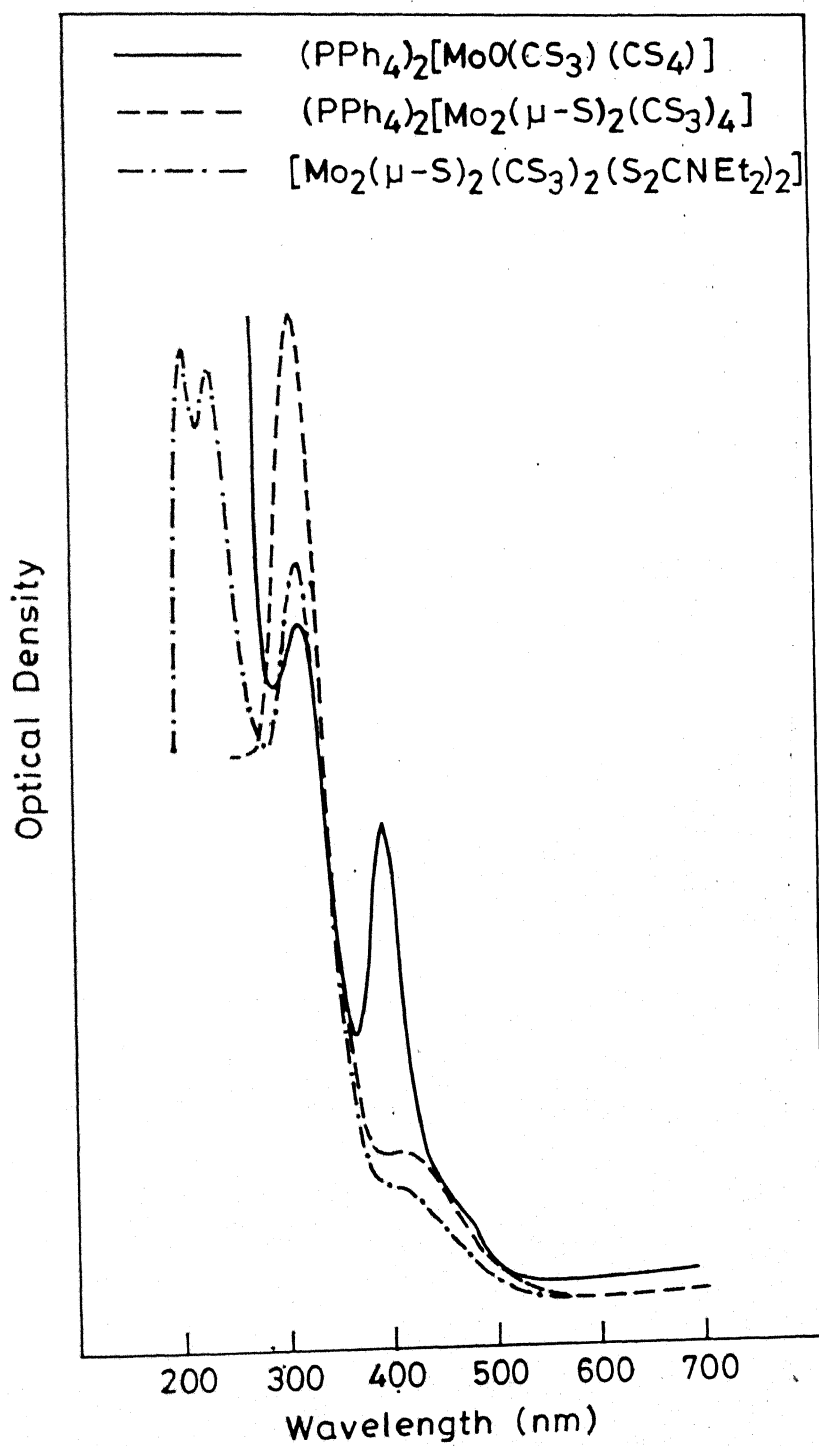


FIG. 4.1.16 ELECTRONIC SPECTRA.

Table 4.5 Electronic Spectral Data

Compound	Solvent	λ_{\max} (nm)	Ref
$(PPh_4)_2[MoS(CS_4)_2].DMF$	DMF	430, 334	73
$(PPh_4)_2[MoO(CS_4)(CS_3)]$	CH ₃ CN	390, 310	This Work
$(PPh_4)_2[Mo_2(\mu-S)_2(CS_3)_4]$	CH ₃ CN	412, 310	-do-
$[Mo_2(\mu-S)_2(CS_3)_2(S_2CNET_2)_2]$	CH ₃ CN	410, 312 230	-do-
$(Et_4N)_2[MoS(S_4)_2]$	DMF	470(sh), 405(sh) 340, 316	31
$(Et_4N)_2[MoO(S_4)_2]$	DMF	555, 475 316	-do-
$(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]$	CH ₃ CN	400, 338 310	-do-
$(Et_4N)_2[Mo(S_2C_2(COPh)_2)_3]$	CH ₃ CN	587, 406 325	-do-
$(PPh_4)_2[Mo(S_2C_2(COOCH_3)_2)_3]$	CH ₂ Cl ₂	650, 450 356	49
$(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$	DMF	600, 448	48
$[MoO(S_2CNET_2)_2(S_2)]$	CH ₃ CN	572, 390 260	This Work
$[MoO(S_2CNET_2)_2Cl]$	CH ₃ CN	520, 455, 442 390, 270	-do-
$(Et_4N)_2[Mo_2OS(\mu-S)_2(S_2)_2]$	CH ₃ CN	550, 475 410	-do-
$((n-Bu)_4N)_2[Mo_2OS(\mu-S)_2(S_2)_2]$	CH ₃ CN	475, 390, 305 233, 273	24
$(Me_4N)_2[Mo_2O_2(\mu-S)_2(S_2)_2]$	CH ₃ CN	463, 377 305, 278	52
$(PPh_4)_2[Mo_2S_2(\mu-S)_2(S_2)_2]$	CH ₃ CN	573, 467 295	14

Table 4.6 Electronic Spectral Data of Dimeric [Mo(VI)-S] Complexes

Compound	Solvent	$\lambda_{\max}(\text{nm})$	Ref
$(\text{AsPh}_4)_2[\text{Mo}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	590, 485 400, 360	This work
$(\text{Et}_2\text{NH}_2)_2[\text{Mo}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	590, 485 400, 360	-do-
$(\text{Et}_4\text{N})_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	DMF	522, 432 392	84
$(\text{AsPh}_4)_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	525, 432 390	This work
$(\text{PPh}_4)_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	522, 432 392	-do-
$(\text{MeNH}_2)_2[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	527, 432 392	-do-
$(\text{PPh}_4)_2[\text{W}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	450, 370 337	-do-
$(\text{PPh}_4)_2[\text{W}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	450, 370 330	86
$(\text{AsPh}_4)_2[\text{W}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	550, 470 370, 340	This work
$(\text{PPh}_4)_2[\text{W}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]$	CH_3CN	550, 470 370, 340	25

synthesized similar tris(dithiolene) complexes of W(IV) and Mo(IV) with different substituents, where similar discrepancy has been observed [100].

Coucouvanis and coworkers have reported the electronic spectra of $[\text{MoS}_9]^{2-}$ and $[\text{MoOS}_8]^{2-}$ [31]. The band maxima of $[\text{MoOS}_8]^{2-}$ prepared in the present study matches with the reported one. In $(\text{S}_4)^{2-}$ coordinated complexes, the band at longer wavelength has been assigned to $(\text{S}_4)^{2-} \rightarrow \text{Mo}$ charge transfer transition. Interestingly, when $(\text{CS}_4)^{2-}$ group is coordinated, this band shifts to higher energy [Table 4.6]. The Mo(IV) complex, $[\text{MoO}(\text{CS}_4)(\text{CS}_3)]^{2-}$, contains three dissimilar groups attached to Mo and hence it is extremely difficult to assign the bands (Fig. 4.1.16). The pentavalent dimer $[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_4]^{2-}$ shows similar electronic spectrum suggesting that the origin of these bands should be of charge transfer type from $(\text{CS}_4)^{2-} / (\text{CS}_3)^{2-} \rightarrow \text{Mo}$. In the neutral dimeric complex, the extra band at 230 nm is due to the internal ligand charge transfer of the coordinated dithiocarbamate [94].

4.1.3 EPR Studies

Electron spin resonance spectra were obtained on a Varian E-109 EPR system (X-band) using DPPH as calibrant. One electron participation of Mo center can be readily monitored by electron paramagnetic resonance spectroscopy where a pentavalent monomeric species readily display the characteristic six line spectrum [101].

Reaction mixture of $(\text{NH}_4)_2\text{MoS}_4$ and CS_2 within
10 min in DMF at room temperature

Microwave power 2mW; Frequency 9.41GHz;
Gain 2×10^3

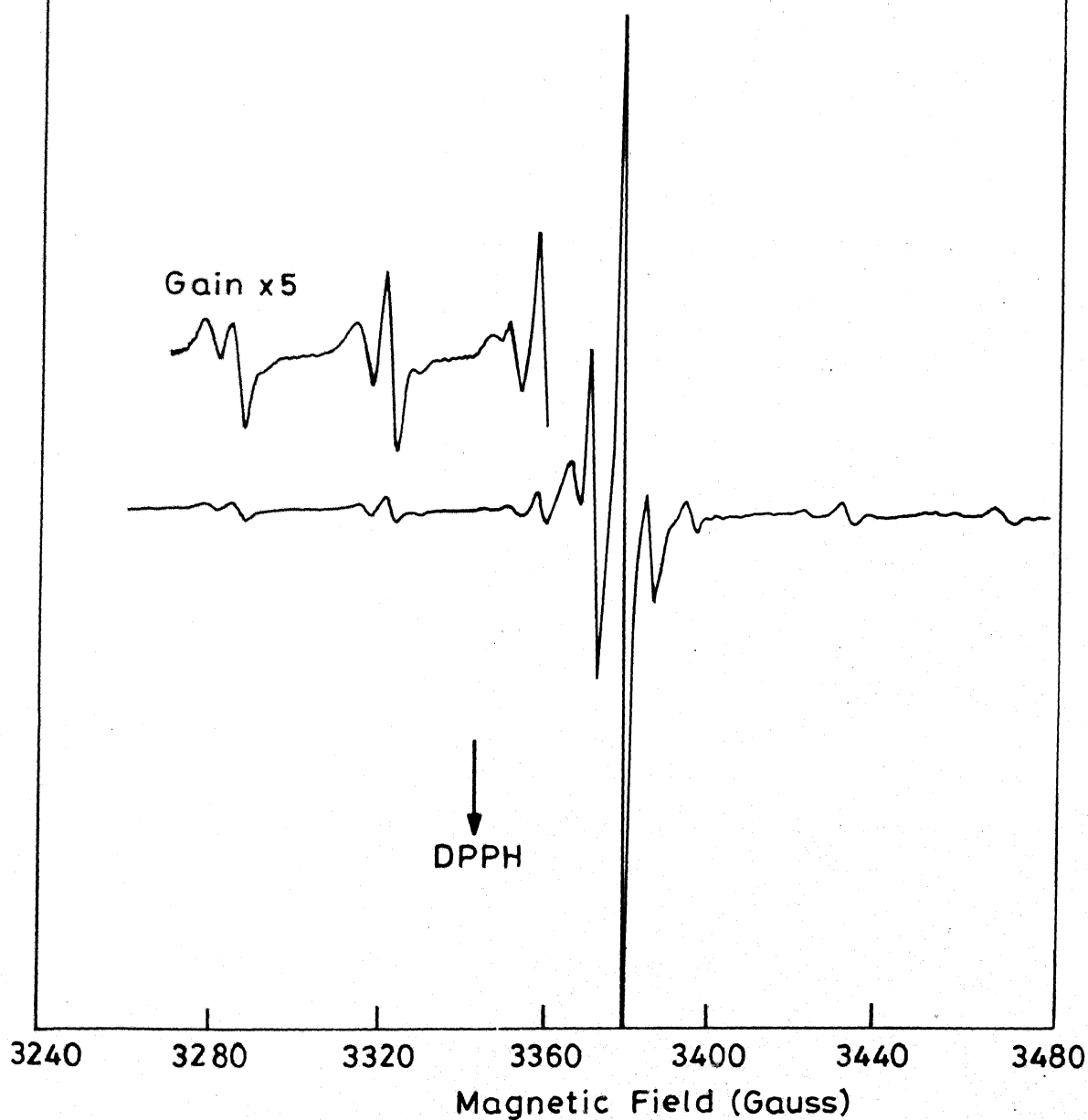


FIG. 4.1.17 EPR SPECTRA.

Reaction mixture of $(\text{Et}_2\text{NH}_2)_2\text{MoS}_4$ and CS_2 within
10 min in DMF at room temperature

Microwave power 2mW; Frequency 9.41GHz ; Gain 2.5×10^3

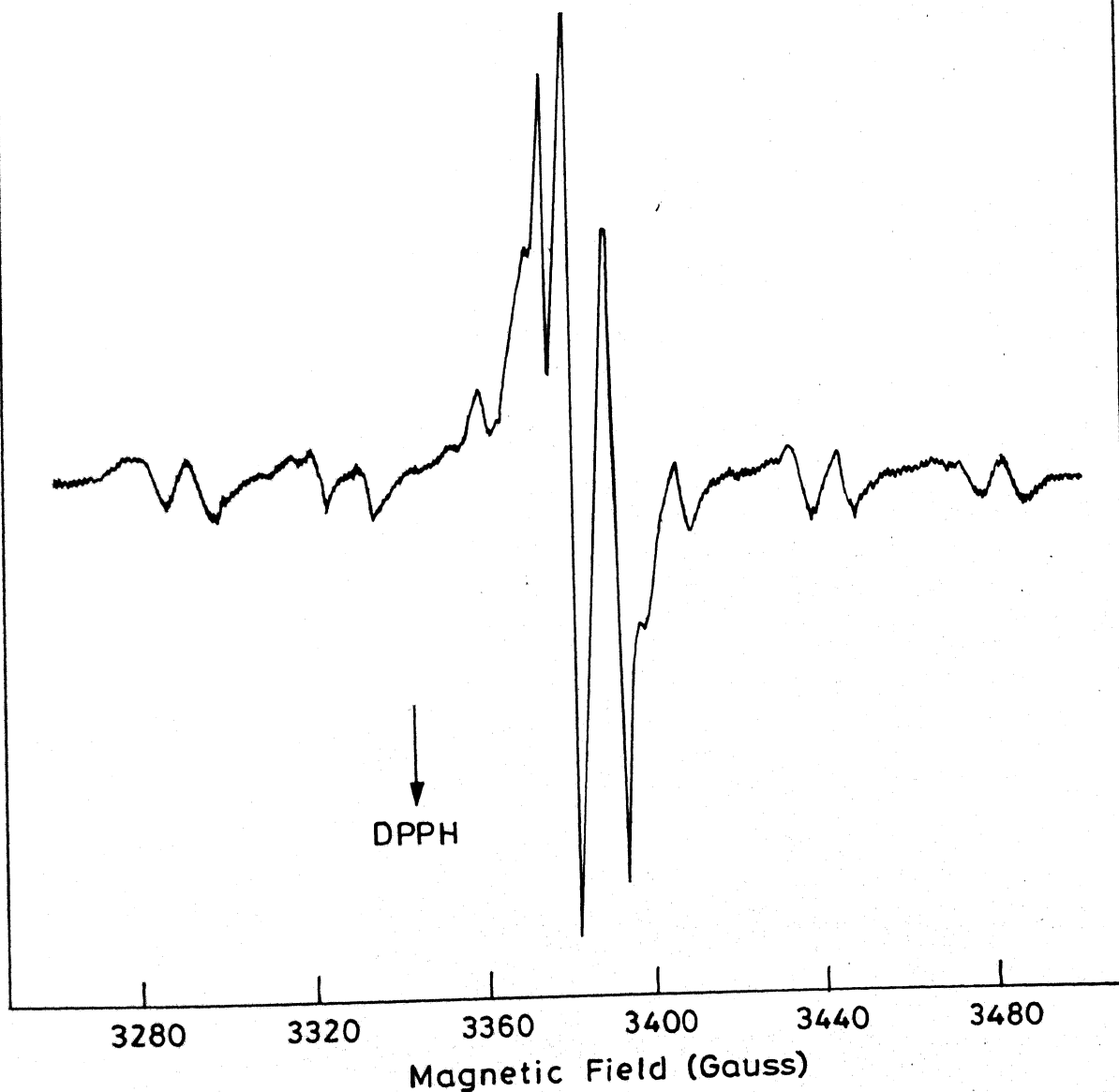


FIG. 4.1.18 EPR SPECTRUM.

Reaction mixture of $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$ and CS_2
within 10 min, in DMF at room temperature.

Microwave power 50 mW; Frequency 9.42 GHz;
Gain 2×10^4

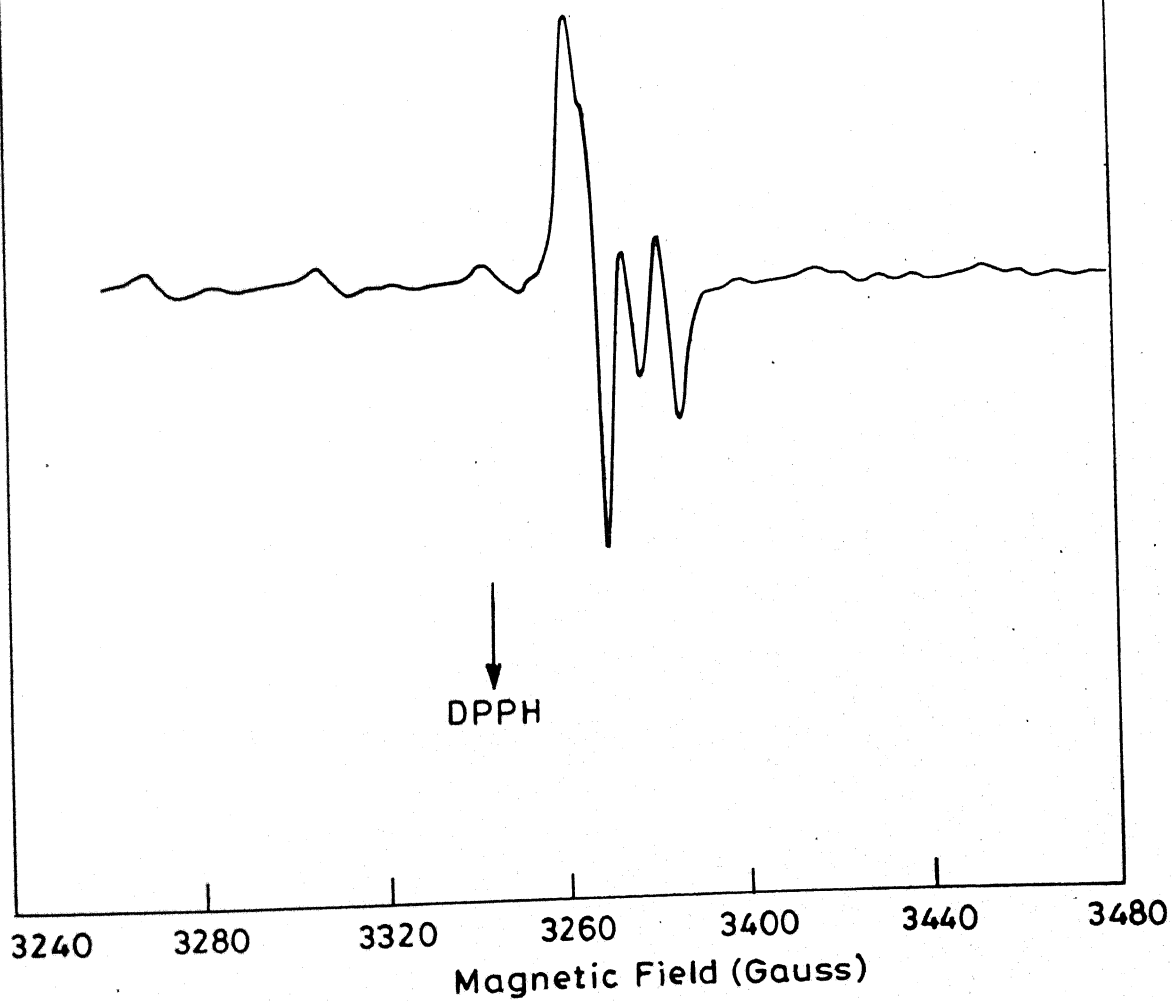


FIG. 4.1.19 EPR SPECTRUM.

A solution of $(\text{NH}_4)_2\text{MoS}_4$, $(\text{Et}_2\text{NH}_2)_2\text{MoS}_4$ or $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$ in DMF with CS_2 gives EPR spectra suggesting the formation of an intermediate monomeric pentavalent Mo species as shown in Figs. 4.1.17 - 4.1.19 ($\langle g \rangle = 1.982; 1.984; 1.976$ respectively). An interesting observation of this spectrum is the splitting of all the six lines into a doublet where the possibility of the formation of two different pentavalent species may be presumed. It is interesting to note that the non-protonated cationic salt of thiomolybdate, CS_2MoOS_3 does not give any EPR signal characteristic of the formation of Mo(V) as an intermediate species, when CS_2 is used. In the preparative procedure we have already seen that this salt reacts with CS_2 to produce $[\text{MoO}(\text{CS}_3)(\text{CS}_4)]^{2-}$ which contains Mo(IV). Thus the involvement of protonated salt does produce a monomeric Mo(V) intermediate species suggesting the involvement of proton participation in these reactions. The formation of {Mo - SH} group from {Mo = S} by proton participation is reminiscent of Xanthine Oxidase system where superhyperfine splitting due to the presence of H atom has been observed [102, 103]. Thus the splitting of the six line spectrum as observed earlier could be due to the participation of a superhyperfine coupling to a single H atom, in which case the EPR active species may be represented as $[(\text{S}_2)\text{Mo(V)}(\text{SH})(\text{S})\text{L}]$, (L = solvent). Recently one proton superhyperfine coupling with $\text{MoO}(\text{OH})$ center has been reported [104].

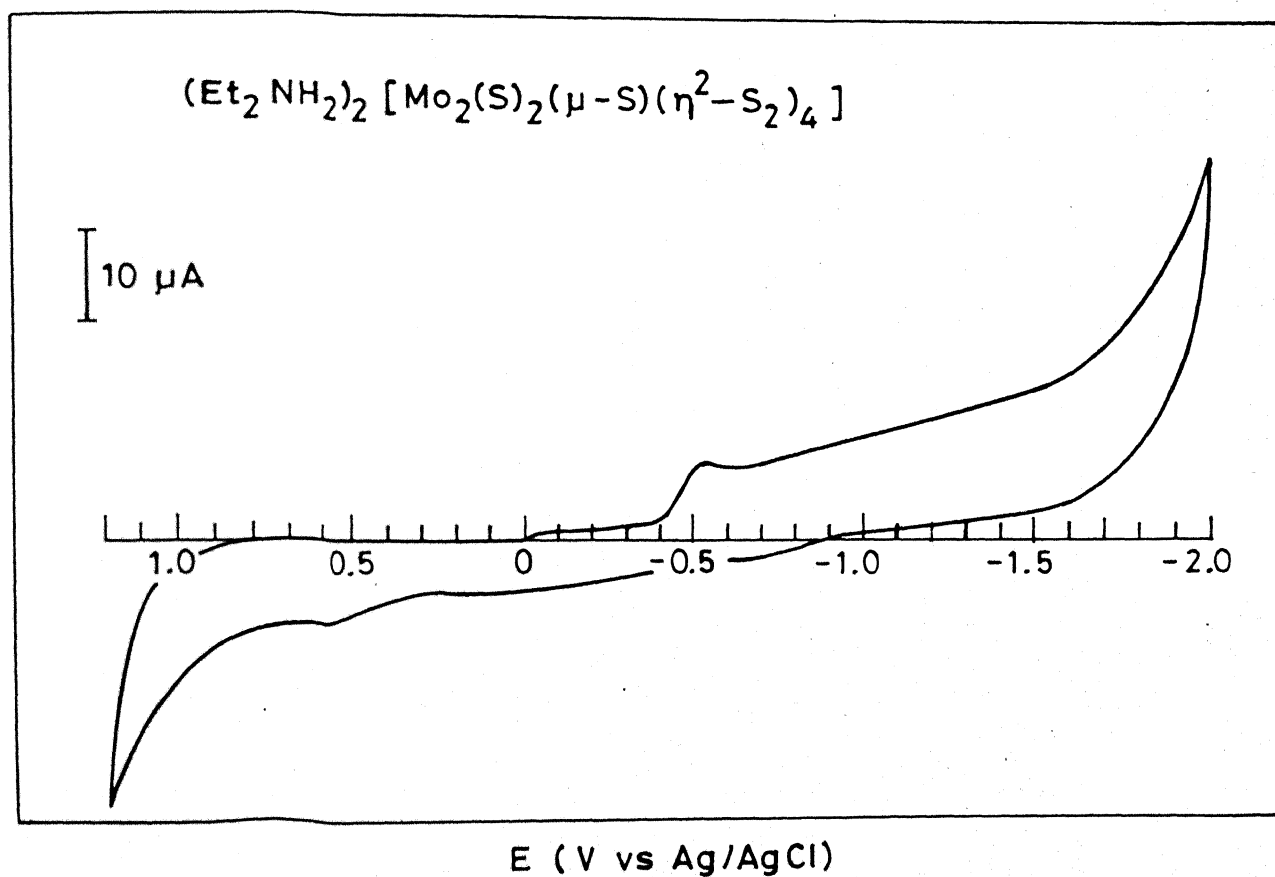
4.1.4 Electrochemistry :

Voltammetric measurements were done on BAS 100 Electrochemical analyzer, and the results were plotted on Houston instruments HIPLOT DMA 40 series digital plotter and BAS printer. All experiments were done under dinitrogen atmosphere in a three electrode configuration using glassy carbon working electrode in positive and negative potential region. All the results were collected at 298°K and referenced to either saturated calomel electrode (SCE) or Ag / AgCl electrode. The reported values are uncorrected for junction potentials.

Recently it has been reported that $(\text{NH}_4)_2\text{MoS}_4$ exhibits an irreversible reduction at -1.80 V in aqueous medium [105]. However in DMF, $(\text{Et}_4\text{N})_2\text{MoS}_4$ shows an irreversible reduction at -2.46 V using Pt working electrode and a reversible one electron reduction at -2.50 V using vitreous carbon electrode [106]. In this work, the electrochemistry of various thiometalates has been studied to understand the difference in the reactivity of protonated and non protonated cationic salts of $[\text{MoS}_4]^{2-}$ and the results are given in Table 4.7. Cesium salt of $[\text{MoOS}_3]^{2-}$ or $[\text{MoS}_4]^{2-}$ undergo irreversible oxidation at +0.237 V and 0.223 V respectively. The cesium salts did not show any reduction up to -2.0 V. Interestingly, when protonated cationic salts like $[(\text{Me})_2\text{NH}_2]_2\text{MoS}_4$ are used the oxidative scan potential drops to +0.165 V meaning thereby, protonated cation facilitates the oxidation of the coordinated sulfur.

Similarly, even in aprotic medium, the protonated cationic salt $(\text{NH}_4)_2\text{MoS}_4$ undergoes reduction at a lower negative potential (-1.8 V) compared to $(\text{Et}_4\text{N})_2\text{MoS}_4$. The salts, $(\text{Me}_2\text{NH}_2)_2\text{MoS}_4$ and $(\text{Me}_2\text{NH}_2)_2\text{MoOS}_3$ undergo irreversible reduction at -1.3 V and at -1.4 V respectively (Table 4.7). This result is well in agreement with the earlier observation that increasing oxygen substitution in the place of sulfido group results in the more negative reduction potential [107, 108].

The all sulfur complexes in the series, $[\text{M}_2(\text{L})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{L} = \text{O}, \text{S}$) i.e. $[\text{M}_2(\text{S})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ are also easily reducible compared to their oxo analogs, $[\text{M}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ (Table 4.7). In general, the molybdenum complexes are easily reducible than their tungsten counterparts. The anodic peak potential is almost non variant for all the anions, presumably due to the oxidation of disulfido group, $(\text{S}_2)^{2-}$. The reduction step involved in higher negative potentials in the case of $(\text{XPh}_4)_2[\text{M}_2(\text{L})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ [$\text{X} = \text{P}$ or As ; $\text{M} = \text{Mo}, \text{W}$; $\text{L} = \text{O}, 2$] is due to the cation, which has been confirmed by using simple $[\text{XPh}_4]^+$ salts. The shift of the reduction potential value to more negative potential in tungsten complexes compared to their molybdenum analogs is expected for metal based reduction processes [23, 109]. Some of the redox peak potentials in the CV study have been checked by Differential Pulse Polarography (DPP) and the values are given in Table 4.7. The cyclic voltammograms of some of the hexavalent dimeric complexes are reproduced in Figs. 4.1.20 - 4.1.22.



Scan rate 100 mV s^{-1}

FIG. 4.1.20 CYCLIC VOLTAMMOGRAM.

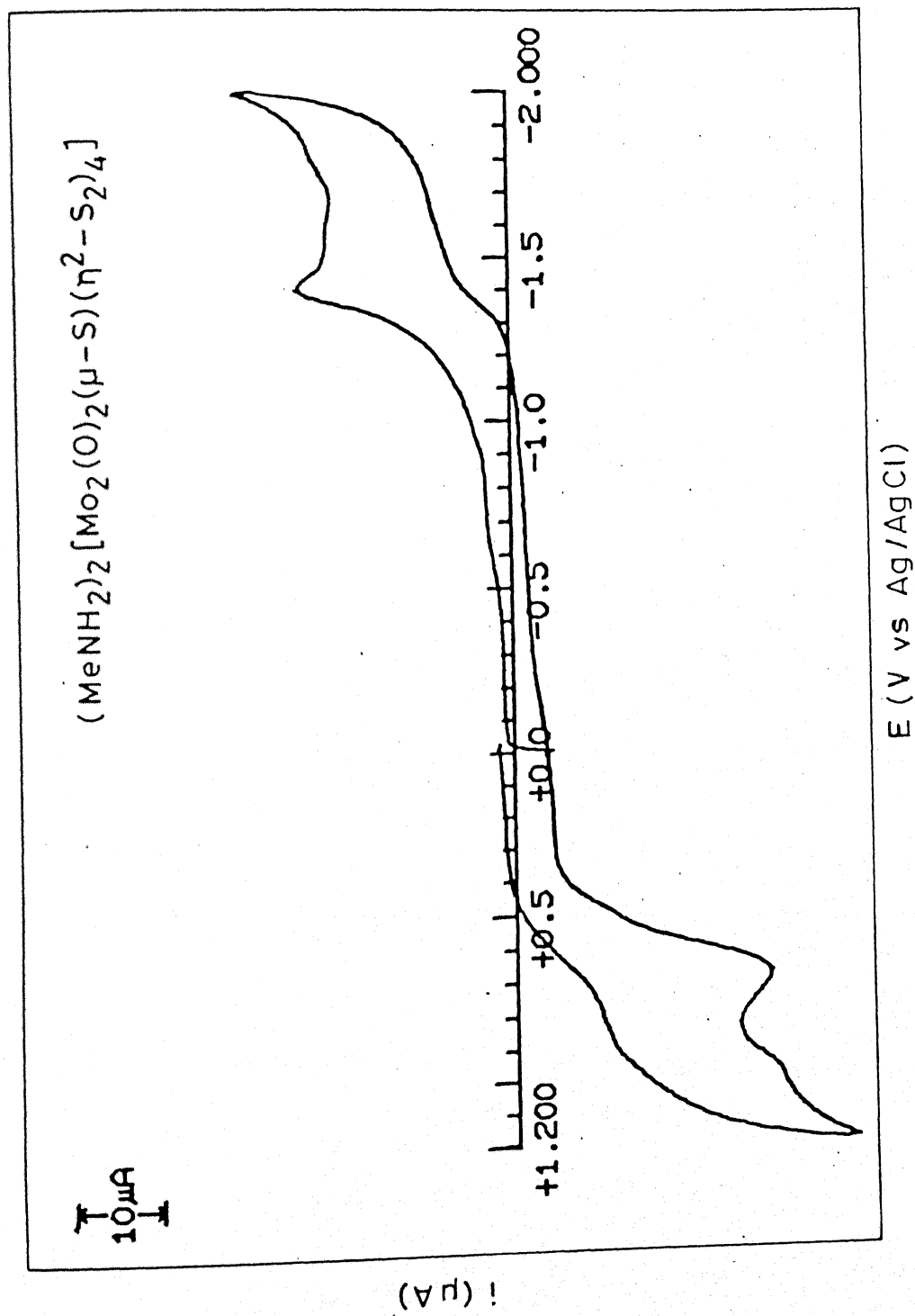


FIG. 4.1.21 CYCLIC VOLTAMMOGRAM.

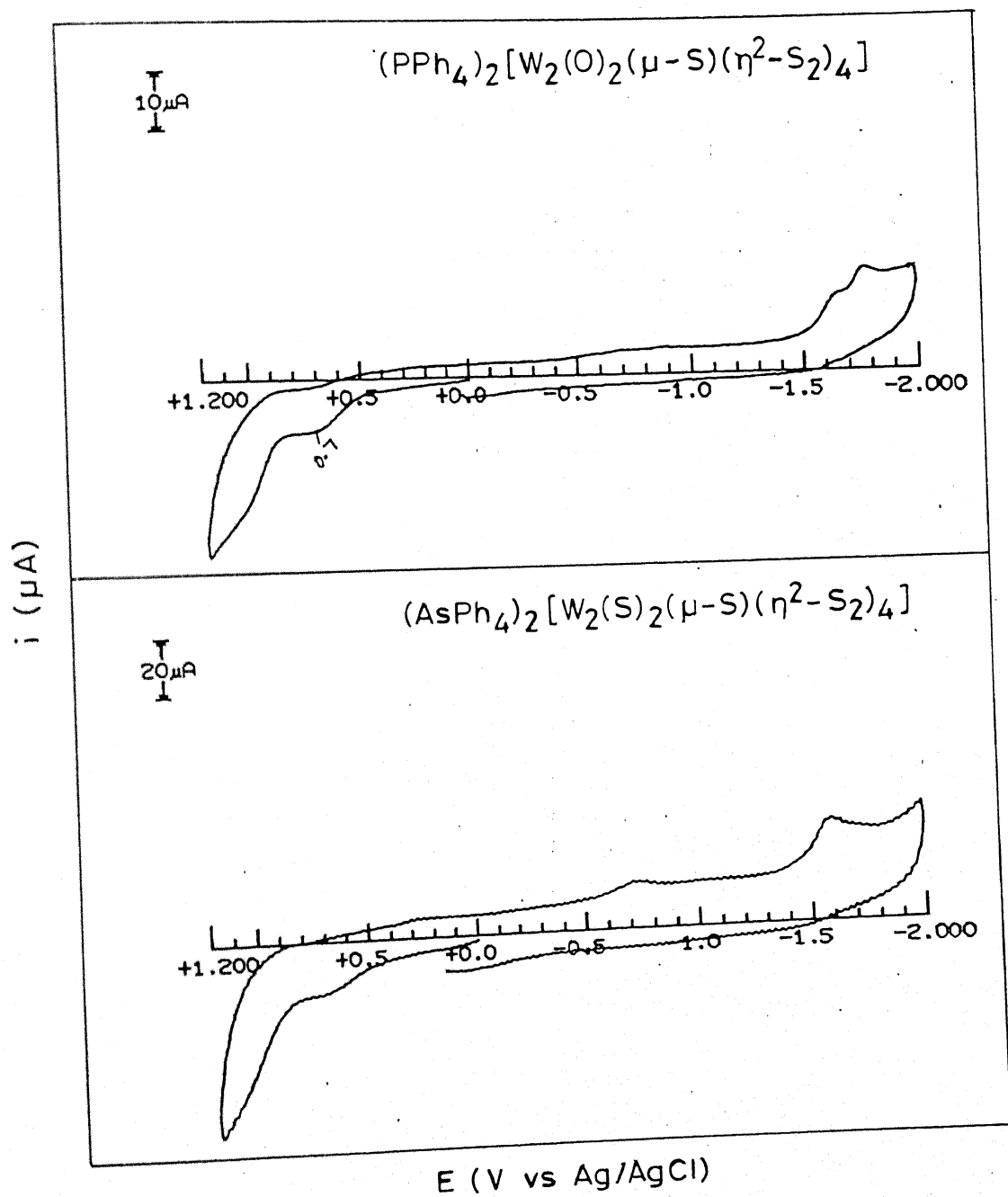


Table 4.7 Electrochemical Data

Compound	$E_{p_c}(V)$	$E_{p_a}(V)$	DPP (V)	
$(Me_2NH_2)_2MoOS_3^*$	-1.400	--	----	
$(Me_2NH_2)_2MoS_4^*$	-1.300	+0.165	----	
$Cs_2(MoOS_3)^*$	--	+0.254	----	
$Cs_2(MoS_4)^*$	--	+0.225	----	
$(Me_2NH_2)_2[Mo_2(O)_2(\mu-S)(S_2)_4]$	-1.400	+0.690		
$(PPh_4)_2[Mo_2(O)_2(\mu-S)(S_2)_4]$	-1.400 -1.840	+0.700	-1.348, +0.580	-1.700
$(Et_2NH_2)_2[Mo_2(S)_2(\mu-S)(S_2)_4]$	-0.520	+0.550	-0.460	
$(AsPh_4)_2[Mo_2(S)_2(\mu-S)(S_2)_4]$	-0.650 -1.660	+0.600	-0.640, +0.540	-1.540
$(PPh_4)_2[W_2(O)_2(\mu-S)(S_2)_4]$	-1.620 -1.755	+0.700	-1.560, +0.600	-1.680
$(AsPh_4)_2[W_2(S)_2(\mu-S)(S_2)_4]$	-0.730 -1.550	+0.640	-0.820, +0.580	-1.500

scan rate = 100 mVs^{-1} (CV), 20 mVs^{-1} (DPP);

0.10M $[(C_2H_5)_4N]ClO_4$; Volts vs Ag/AgCl

* 0.10M $(n-Bu_4N)BF_4$; Volts vs SCE

The hexacoordinated $[\text{Mo}(\text{dithiolene})_3]^{2-}$ complex shows irreversible reduction at -1.645 V (vs Ag / AgCl) and the pentacoordinated $[\text{MoO}(\text{dithiolene})_2]^{2-}$ complex (Fig. 4.1.23) at -1.76 V (vs SCE) (Table 4.8). The dithiolene ligands are generally known to occur in several electron population for which facile reversible redox chemistry has been observed on the metal as well as ligand center or a combination of both [92, 110]. Hence, for the tris(dithiolene) complex it is somewhat surprising that no reversible redox process takes place under the time scale of CV study. In the oxidative scan the large, difference in E_{p_a} value between the pentacoordinated and hexacoordinated species suggest that the oxo species can be oxidized more readily compared to the tris(dithiolene) species.

While this work was in progress, a detailed electrochemical study of the compound $[\text{MoO}(\text{S}_2\text{CNET}_2)_2(\text{S}_2)]$ and related W compounds has been done by Broomhead and coworkers [111]. In their CV study at Hg electrodes, they have observed a very unusual oxidation process where $(\text{dtc})^-$ and $(\text{S})^{2-}$ are released. With glassy carbon electrode, we could not find any electroactive species in the oxidative scan. We attribute the decomposition of the said complex in their study to the use of the Hg electrode which is a potential reactant to abstract the coordinated $(\text{dtc})^-$ from the complex. In our study, we have observed two irreversible reduction peaks at -0.820 V and -1.460 V. The DPP also shows similar reduction reactions (-0.740 V and -1.340 V) (Fig. 4.1.24; Table 4.8). The pentavalent monomeric compound, $[\text{MoO}(\text{S}_2\text{CNET}_2)_2\text{Cl}]$,

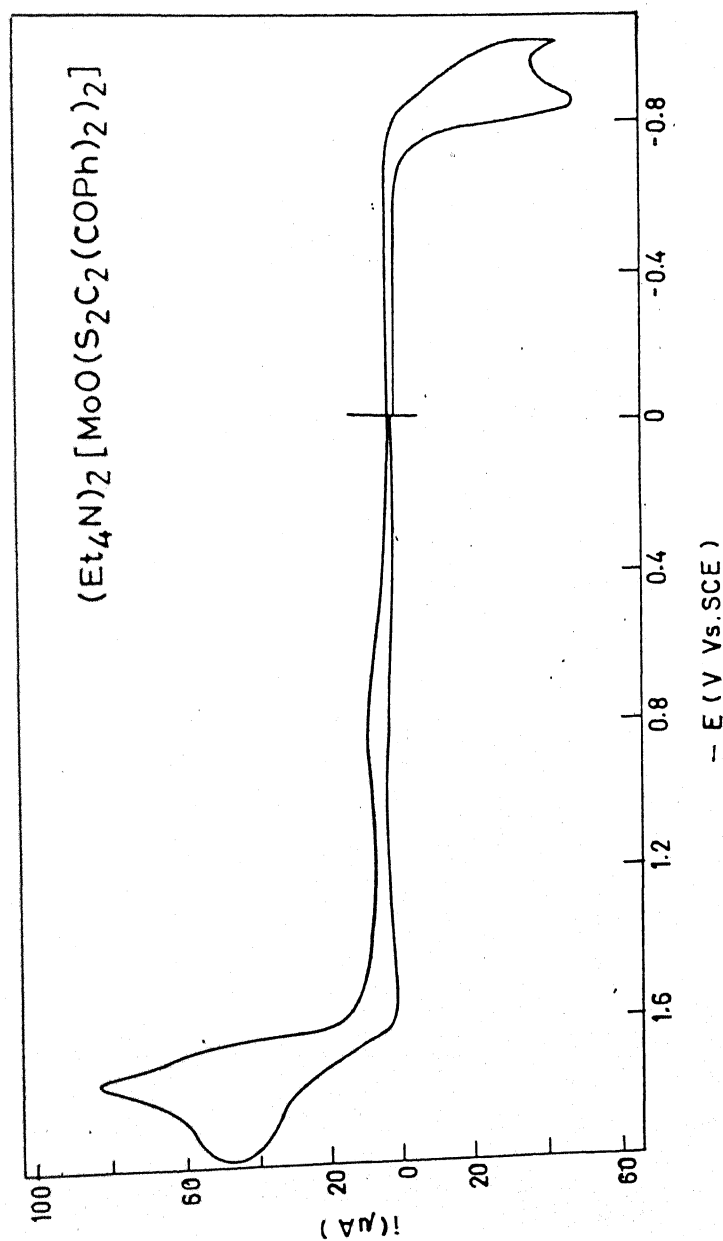
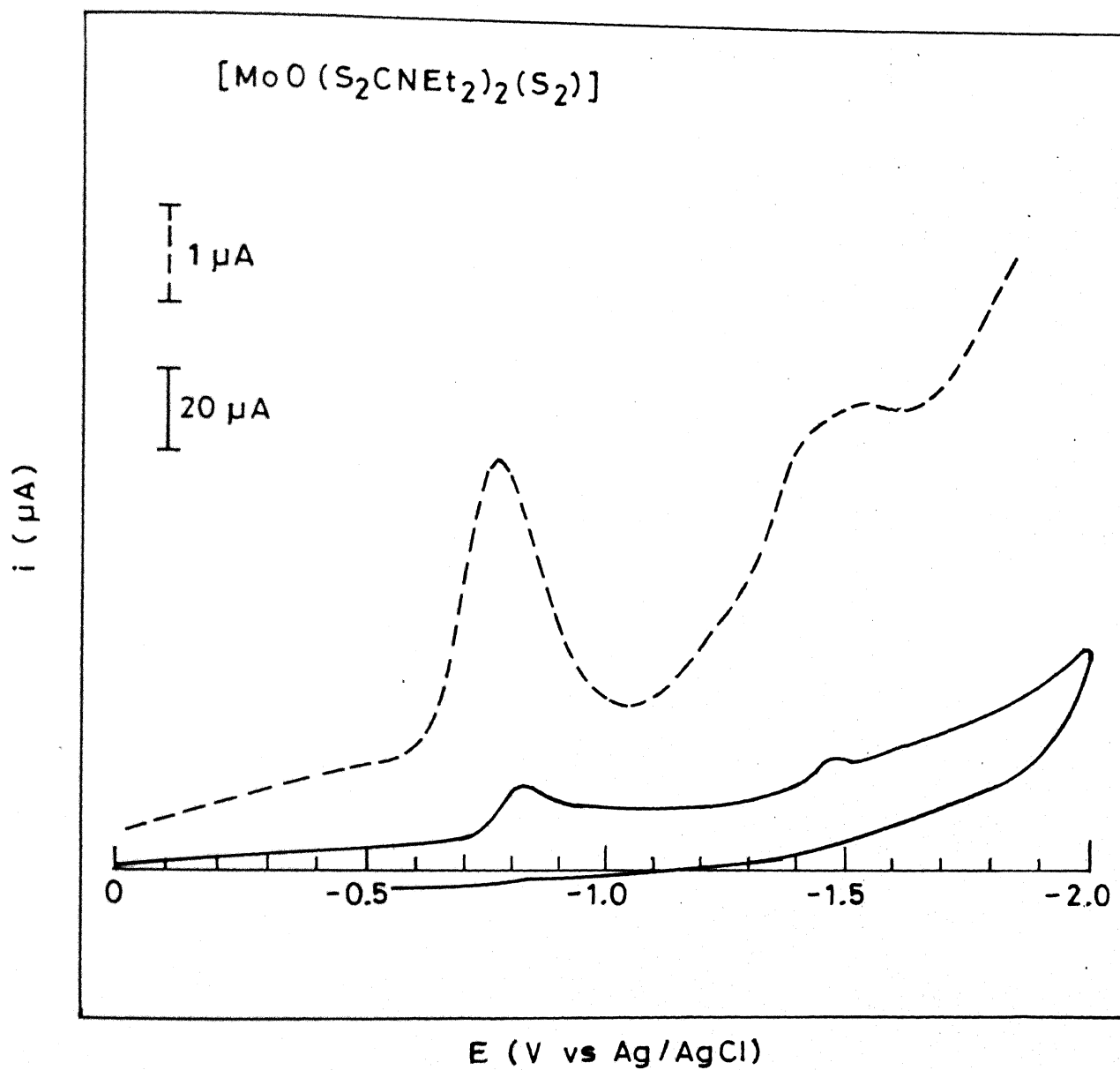
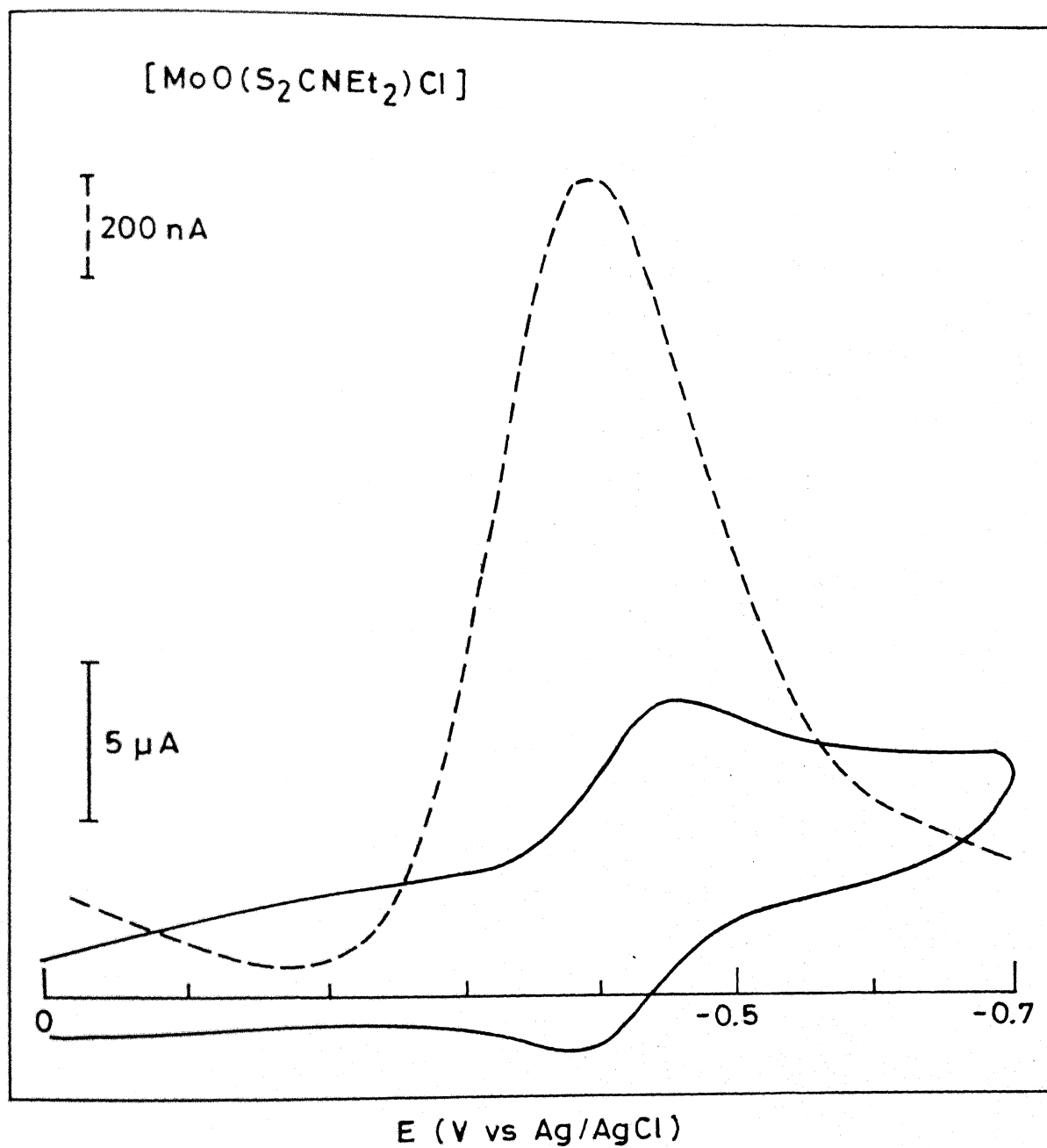


FIG. 4.1.23 CYCLIC VOLTAMMOGRAM.



Scan rate 100 mVs^{-1} (CV); 20 mVs^{-1} (DPP)

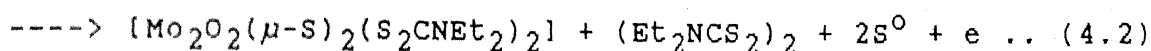
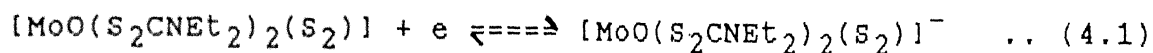
FIG. 4.1.24 CYCLIC VOLTAMMOGRAM AND DIFFERENTIAL PULSE POLAROGRAPH.



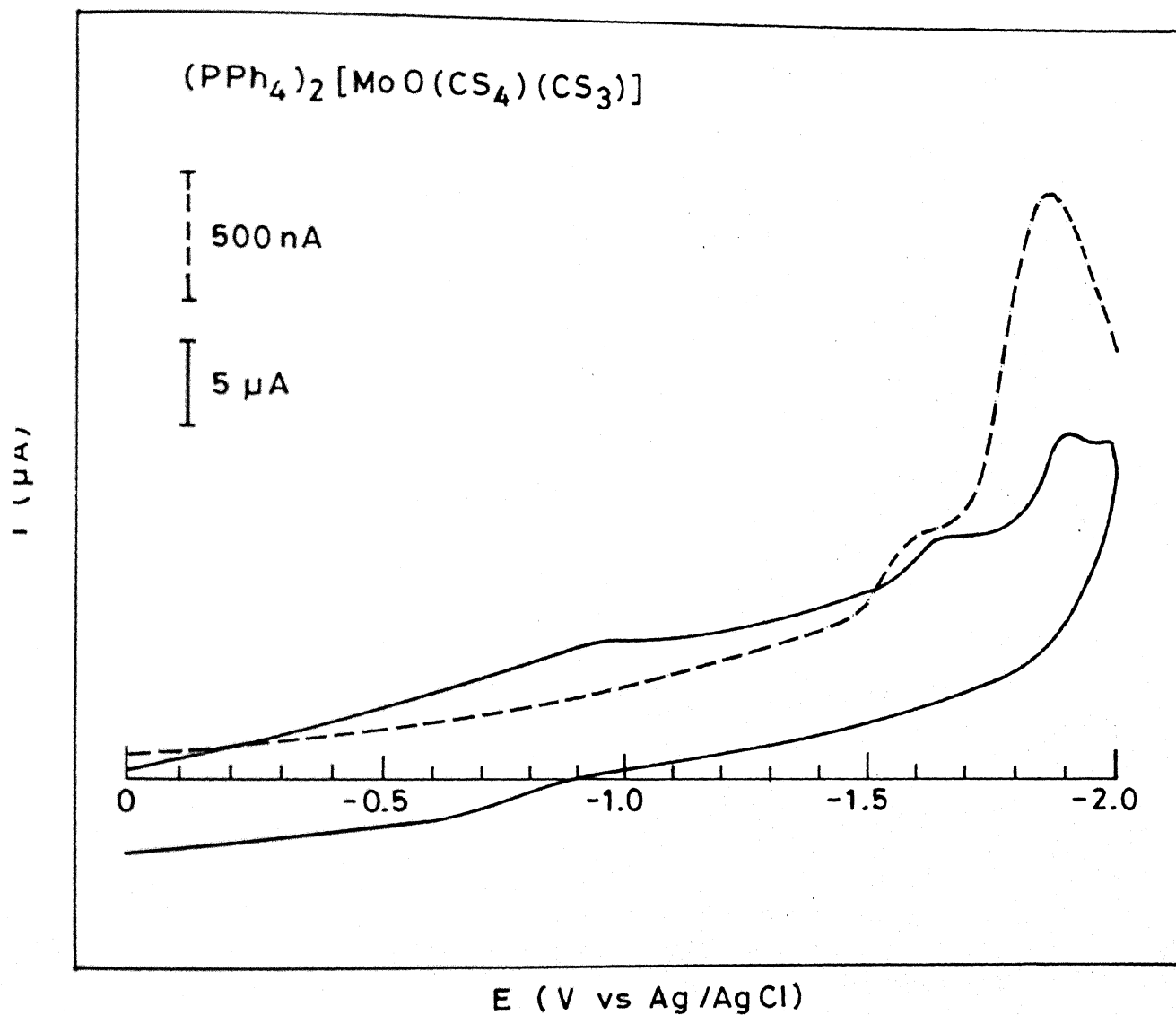
Scan rate 100 mVs^{-1} (CV); 20 mVs^{-1} (DPP)

FIG.4.1.25 CYCLIC VOLTAMMOGRAM AND DIFFERENTIAL PULSE POLAROGRAPH.

with almost similar ligands shows reversible reduction at -1.22 V. (Fig 4.1.25, Table 4.8) . Comparing this value, the more negative peak potential at -1.460 V for $[\text{MoO}(\text{S}_2\text{CNET}_2)_2(\text{S}_2)]$ may be due to the reduction of Mo(VI) to Mo(V). The irreversible reduction at -0.82 V could be assigned to the reduction of the coordinated $(\text{S}_2)^{2-}$ group, which may be represented as follows.



The monomeric $[\text{MoO}(\text{CS}_4)(\text{CS}_3)]^{2-}$ shows an irreversible reduction at -1.628 V in both CV and DPP studies. At a higher negative potential the compound exhibits a second irreversible reduction which can be attributed to the reduction of $(\text{PPh}_4)^+$ cation. In the oxidative scan, the compound undergoes an irreversible oxidation at a high positive potential (1.79 V). This high value is indicative of the stability of the Mo(IV) species towards oxidation. The dimeric complex $[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_2(\text{dtc})_2]$ undergoes irreversible reduction at -1.27 V, which suggests the extra stability of the dimeric species, compared to the pentavalent monomeric complex, $[\text{MoO}(\text{S}_2\text{CNET}_2)_2\text{Cl}]$ where one electron reversible reduction occurs at -0.448 V. The irreversible reduction shown by the complex $(\text{PPh}_4)_2[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_4]$ at -1.73 V may be due to the reduction of $(\text{PPh}_4)^+$ cation. The complex undergoes a reversible reduction at -1.2 V. This can be attributed to one electron transfer reaction with the formation of a mixed valence



Scan rate 100mVs^{-1} (CV); 20mVs^{-1} (DPP)

Fig.4.1.26 CYCLIC VOLTAMMOGRAM AND DIFFERENTIAL PULSE POLAROGRAM.

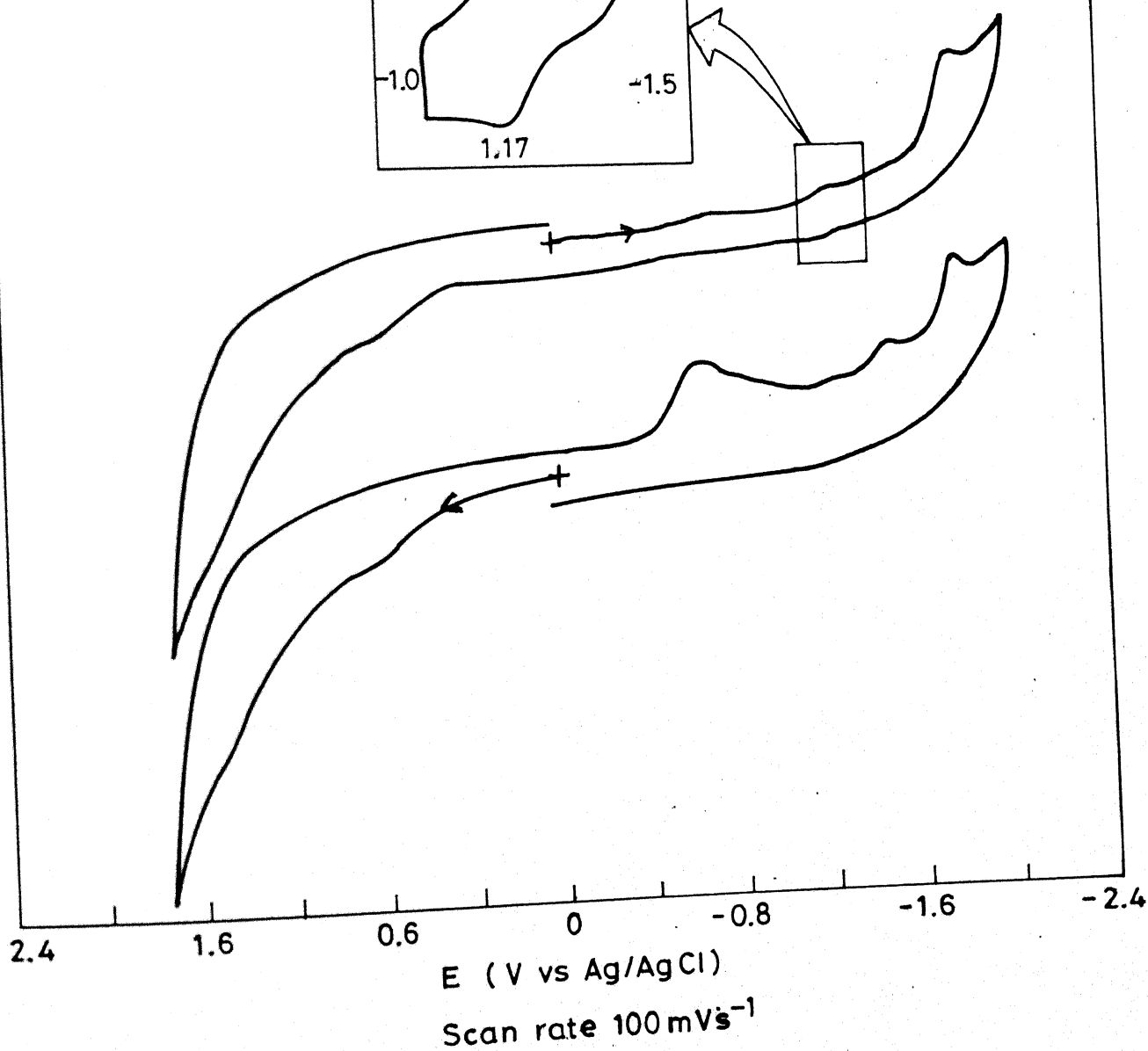
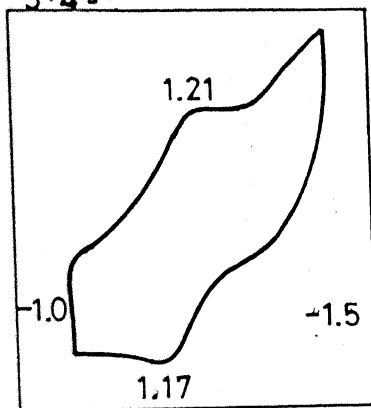
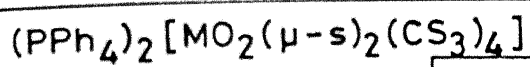


FIG. 4.1.27 CYCLIC VOLTAMMOGRAMS.

Table 4.8 Electrochemical Data

Compound	$E_{p_c}(V)$	$E_{p_a}(V)$	DPP (V)
$(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]^*$	-1.760	+0.840	---
$(Et_4N)_2[Mo(S_2C_2(COPh)_2)_3]$	-1.645	+1.668	---
$[MoO(S_2CNet_2)_2(S_2)]$	-0.820 -1.460	--- ---	-0.740 -1.340
$[MoO(S_2CNet_2)_2Cl]$	-0.448 ^r	+1.122 ^r	-0.360 +1.120
$(PPh_4)_2[MoO(CS_4)(CS_3)]$	-1.628 -1.911	+1.790	-1.600 -1.850
$[Mo_2(\mu-S)_2(CS_3)_2(S_2CNet_2)_2]$	-1.270	+1.360	-1.200
$(PPh_4)_2[Mo_2(\mu-S)_2(CS_3)_4]$	-0.560 -0.680 -1.210 ^r -1.730	+0.780	---

scan rate = 100 mVs⁻¹ (CV), 20 mVs⁻¹ (DPP);

0.10M $[(C_2H_5)_4N]ClO_4$; Volts vs Ag/AgCl

* 0.10M (n-Bu₄N)BF₄ ; Volts vs SCE

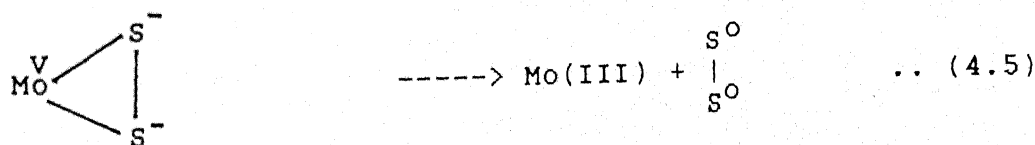
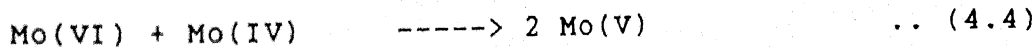
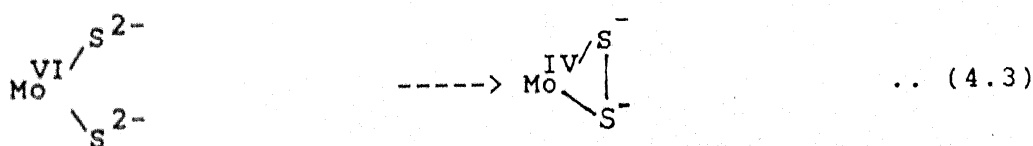
r reversible

oligomeric Mo species. Apart from this reversible wave, two irreversible reductions at -0.56 V and 0.68 V are observed in the reductive scan (Fig. 4.1.27). In the oxidative scan, the current density of these two peaks increases suggesting that some oxidized species are responsible for these peaks.

4.2 Reactivity of {Mo=S} bond in $[\text{MoS}_4]^{2-}$:

4.2.1 Aging of $(\text{NH}_4)_2\text{MoS}_4$

The formation of the dinuclear complex $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ on aging of simple tetrathiomolybdate is a remarkable reaction. When the formation of the same complex was first reported by Müller et al from an aqueous solution of $[\text{Mo}_2\text{O}_2\text{S}_2]^{2-}$ it was thought to be redox condensation reaction without the influence of any external agent [51, 52, 112]. They have proposed a mechanism for such reactions which is given in the equations 4.3 - 4.5.

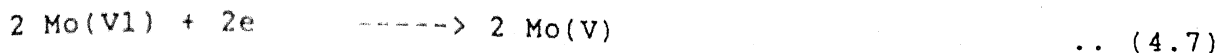
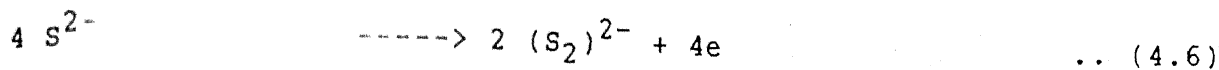


Wedd and coworkers [113] have reported that $[\text{MoOS}_3]^{2-}$ under similar reaction conditions produces multiple products like MoS_2 , $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ and $[\text{Mo}_3\text{OS}_8]^{2-}$. The formation of multiple products in the reaction using $[\text{MoOS}_3]^{2-}$ suggests the formation of Mo(IV) in these redox reactions which furnishes support to the above mechanism. But the point of interest lies in the electron transfer across {Mo=S} bond. It should also be noted that these reactions are catalyzed thermally and the poor yield of the final product does not support a straight forward reaction. The influence of external agents has been ignored in these reactions to bring about such electron transfer processes.

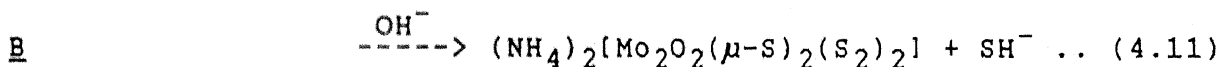
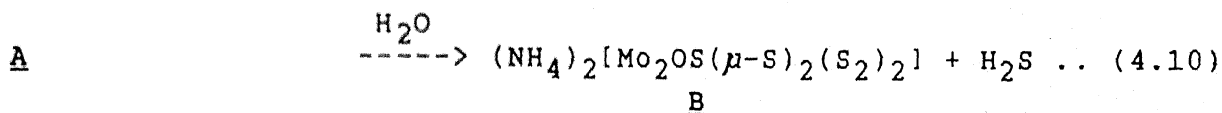
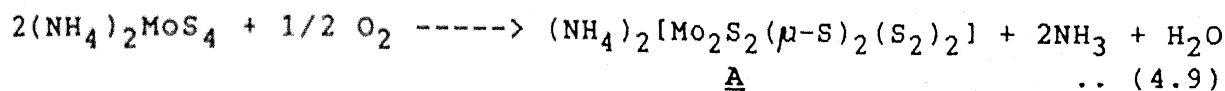
The aging of $(\text{NH}_4)_2\text{MoS}_4$ to produce $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ under aerobic conditions justifies that aerial oxygen contributes for the electron transfer across {Mo=S} bond in $[\text{MoS}_4]^{2-}$. In the limited supply of air, such as when it is stored in the dessicator, the appearance of mauve-brown tinge takes a longer time than when the sample is kept open in the laboratory atmosphere. Since both the experiments were performed at the same temperature, the thermal influence is ruled out. Furthermore, heating of ammonium tetrathiomolybdate, under inert atmosphere to yield MoS_3 as the final product, is well documented in the literature [18]. The reaction of $(\text{NH}_4)_2\text{MoS}_4$ in $(\text{Et}_4\text{N})\text{Br}$ melt under oxygen produces $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ in good yield (70%) suggesting the influence of oxygen to bring about the dimerization of $[\text{MoS}_4]^{2-}$ [78]. It is to be noted that the decomposition of $(\text{NH}_4)_2\text{MoS}_4$ does not

start before 150°C and $(\text{Et}_4\text{N})\text{Br}$ melts at $105\pm 5^{\circ}\text{C}$. Thus the involvement of temperature is not that crucial to bring about the dimerization of $[\text{MoS}_4]^{2-}$ as it is dependent on aerial oxygen. The dimerization can also be brought about by refluxing a mixture of $(\text{NH}_4)_2\text{MoS}_4$ and $(\text{Et}_4\text{N})\text{Br}$ in CH_3OH or CH_3CN in air, to yield $(\text{Et}_4\text{N})_2[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]$. The oxo-sulfido dimer is resistant to hydrolysis in neutral or acidic media but in basic medium changes to $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$. The corresponding all-sulfur compound $(\text{Et}_4\text{N})_2[(\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2)]$ is very susceptible to hydrolysis. When $[\text{MoS}_4]^{2-}$ is refluxed in dry CH_3CN in air and the reaction monitored by electronic spectrum every 5 min for 1 h, the characteristic bands of the all sulfur complex $[\text{Mo}_2\text{S}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ (537, 467, 295 nm) appear 5 min after the start of the reaction. The compound is hydrolyzed to $[\text{Mo}_2\text{OS}(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ as stoichiometric amount of water is produced in the reaction (eqs. 4.9-4.11). When NH_4OH is added to the reaction mixture, the spectrum shows the characteristic bands of $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ [78].

All these reactions mentioned above are examples of internal electron transfer reactions induced by atmospheric oxygen. The external oxidant, oxygen induces intramolecular electron transfer from the sulfido ligands (internal reductant) to the central molybdenum (VI) atom (internal oxidant). The electron balanced reactions for these processes can be written as shown in the equations 4.6 - 4.8.



Thus, the aging of $(NH_4)_2MoS_4$ in air is primarily an induced internal electron transfer reaction caused by atmospheric oxygen followed by stepwise hydrolysis to yield $(NH_4)_2[Mo_2O_2(\mu-S)_2(S_2)_2]$ as shown in the equations 4.9 - 4.11.



The metathesis reaction to prepare $(Et_4N)_2MoS_4$ [114] by stirring $(NH_4)_2MoS_4$ and $(Et_4N)Cl$ in CH_3CN needs to be commented at this point. Unless the reaction is done under inert atmosphere, the compound obtained will not be pure.

Thus the condensation reaction of thiomolybdates differ entirely in relation to similar condensation reaction of oxomolybdate $[MoO_4]^{2-}$. The latter undergoes electrophilic attack under the influence of proton and condensation occurs to yield polymolybdates with molybdenum still in the highest oxidation state i.e +6. With $[MoS_4]^{2-}$ although electrophilic attack of proton takes place, redox condensation occurs. This suggests that the sulfido group gets protonated first and then the aerial

oxygen induces the redox process across {Mo=S} bond. In the case of $[\text{MoOS}_3]^{2-}$ although the electronegativity values suggest that {M=O} bond should be protonated first in preference to the {Mo=S} bond, the isolation of disulfido bridged species and not dioxo bridged species suggest that here also the coordinated sulfido group gets protonated first and not coordinated oxo group. This is very much similar to the reaction in Xanthine Oxidase [115].

4.2.2 Reaction of $(\text{MoS}_4)^{2-}$ with sulfur in the presence of H^+

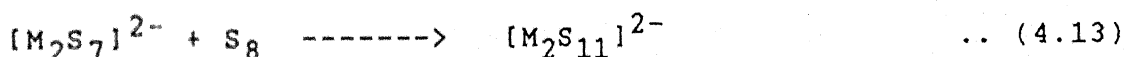
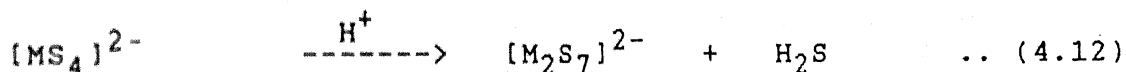
It has already been mentioned in the introductory chapter, that elemental sulfur can induce electron transfer across {Mo=S} bond in thiometallates [31, 43]. However these reactions are very sensitive to temperature, solvent and the counter cation used. For example, $(\text{NEt}_4)_2\text{MoS}_4$ when reacted with elemental sulfur in CH_3CN at ambient conditions yields the sulfur ring complex $(\text{Et}_4\text{N})_2[\text{Mo}^{\text{IV}}\text{S}_9]$ [31]. On the contrary $(\text{NH}_4)_2\text{MoS}_4$ in the presence of elemental sulfur and Et_4NBr in DMF at 95°C affords $(\text{NEt}_4)_2[\text{Mo}_2^{\text{V}}\text{S}_{12}]$ [47]. We have also observed, that the formation of $[\text{MoS}_9]^{2-}$ and $[\text{MoOS}_8]^{2-}$ can be readily achieved from the protonated salts like $(\text{NH}_4)_2\text{MoS}_4$ and $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$ respectively, on treatment with S_8 and Et_4NBr . It should be mentioned here, that the presence of quaternary ammonium salt is essential to get $[\text{MoOS}_8]^{2-}$ from $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$. Interestingly, in the absence of quaternary ammonium salt the course of the reaction proceeds entirely in a different way to yield $[\text{Mo}_2^{\text{VI}}(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$. Thus depending on the reaction conditions $[\text{MoS}_4]^{2-}$ can afford

compounds containing Mo(IV), Mo(V) as well as Mo(VI) on treatment with elemental sulfur.

The reaction between $(\text{PF}_6)[\text{Fe}(\text{C}_5\text{H}_5)_2]$ and $(\text{Et}_4\text{N})_2[\text{MoO}(\text{S}_4)_2]$ has been reported to yield the dinuclear $[\text{Mo}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ and the tetranuclear $[\text{Mo}_4(\text{O})_4(\mu\text{-S})_2(\text{S}_2)_8]^{2-}$ complexes [84]. The dimeric complex has also been synthesized by the nitrosylation of heptamolybdate using hydroxylamine and denitrosylation of $\{\text{M-NO}\}$ moiety under basic conditions [85]. It is well known that the reaction between NH_2OH and $[\text{MoO}_4]^{2-}$ invariably produces $\{\text{M-NO}\}$ moiety where the formal oxidation state of Mo can be best described as +2 [116]. Thus in both the above described methods, isolation of the said compound depends on the oxidation of the reduced molybdenum to molybdenum in hexavalent state. Manoli and coworkers in an attempt to prepare the bis(thiometallate) complex of Mn(II) $[\text{Mn}(\text{WS}_4)_2]^{2-}$, have isolated similar complexes of tungsten such as $[\text{W}_2(\text{S}_2)_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ and $[\text{W}_2(\text{O})_2(\mu\text{-S})(\text{S}_2)_4]^{2-}$ [25, 86]. Though the crystal structure of the latter compound has been done by picking up a suitable crystal from the reaction mixture, no straight forward method has been described for the synthesis of the same.

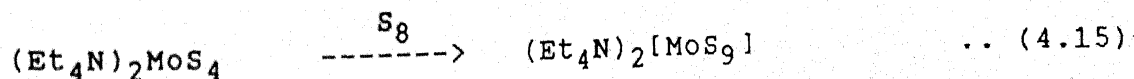
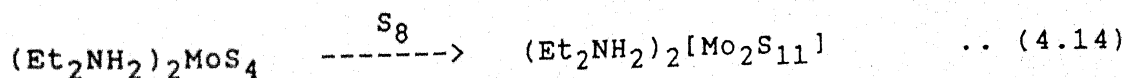
Protonation of the thiometallates as described earlier, invariably produces polythiometallates where at least one of the metal centers is in a reduced oxidation state [27-29]. The versatile reactivity of elemental sulfur with the thiometallates under different reaction conditions prompted us to study the

influence of proton as well as elemental sulfur on the thiometallates. Manoli and coworkers have used similar reaction to isolate $[W_2S_{11}H]^-$ [26]. Here, $(PPh_4)_2WS_4$ has been refluxed with S_8 for 15 min, and then cooling and acidification leads to the said compound. We have tried to observe the reaction of both proton and elemental sulfur together, with the thiometallates. Using this methodology, we have succeeded in isolating the entire series of the hexavalent dimeric complexes of the general formula, $[M_2(L)_2(\mu-S)_2(S_2)_4]^{2-}$ ($M = Mo, W; L = O, S$). Our synthetic rationale is to allow first the protonation of the thiometallates which then react with elemental sulfur to give the desired compounds as shown below.



The formation of $[Mo_2S_7]^{2-}$ during the acidification of aqueous solutions of $[MoS_4]^{2-}$ has been proposed previously on the basis of pH and conductometric titrations [117].

In the present study, it is also of interest to stress that the stoichiometry of the thiometallate and sulfur is not the crucial factor to dictate the course of the reaction. It is the protonated cationic species which drives the reaction resulting in the condensation product as shown in equation 4.14.



The difference in reactivity as described in these two equations (4.14 and 4.15) may be attributed to entirely different course of reactions. In the absence of protons, induced electron transfer takes place across the {Mo=S} bond and the external oxidant S_8 on reduction produces $(S_4)^{2-}$ which stabilizes the generated Mo(IV) [43] at ambient condition. Similar transformation can be brought about in a variety of ways where the oxidation state of the central atom may vary [21, 22, 56, 78]. However for the reaction in the presence of protonated cation or free proton, condensation reaction with dimerization (eq. 4.12) may be the first stage followed by intramolecular electron transfer between the metal-sulfur bond which happens in tungsten-sulfur chemistry [25, 27-29, 47]. In the presence of elemental sulfur the stability of the dimeric condensation product, probably, is achieved by coordination expansion at ambient conditions as shown in eqs. 4.12 and 4.13. The anions $[Mo_2(O)_2(\mu-S)(S_2)_4]^{2-}$ and $[W_2(S)_2(\mu-S)(S_2)_4]^{2-}$ have been found to belong to monoclinic space group [25, 84] whereas $[W_2O_2(\mu-S)(S_2)_4]^{2-}$ belongs to orthorhombic [86]. All the quaternary salts show the presence of one CH_3CN molecule of crystallization as indicated by elemental analysis. The d spacings of the four anions suggest that $[Mo_2(S)_2(\mu-S)(S_2)_4]^{2-}$ may be isostructural to $[W_2(O)_2(\mu-S)(S_2)_4]^{2-}$. The interplanar spacings of the most prominent peaks of these complexes are listed in Table 4.9.

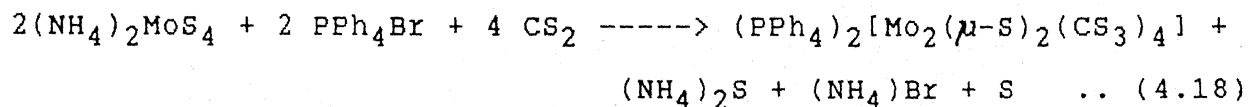
Table 4.9 X- ray Powder Data

Compound	Interplanar d spacings of the most prominent peaks (Å)
$[(PPh_4)_2Mo_2O_2S_9]$	8.0360(s), 6.5532(w), 6.2757(w), 5.5345(m) 5.0922(w), 4.4801(s), 4.2669(m), 4.0367(m) 3.7200(w), 3.3359(w), 3.2176 (w)
$[(PPh_4)_2W_2S_{11}]$	8.1100(s), 6.4114(w), 6.2757(w), 5.7860(w) 5.1510(m), 4.5026(s), 4.3496(w), 4.0550(m) 3.7354(w), 3.3606(w), 3.2291(w)
$[(PPh_4)_2W_2O_2S_9]$	8.1847(s), 6.9100(m), 5.6041(m), 5.0065(w) 4.5026(m), 4.2669(w), 4.0187(w), 3.6896(w) 3.3857(w), 3.2406(w)
$[(PPh_4)_2Mo_2S_{11}]$	8.1100(w), 6.5053(s), 5.4333(m), 5.0348(w) 4.4357(w), 4.3079(m), 3.9309(w), 3.7666(w) 3.3236(w), 3.2063(w)

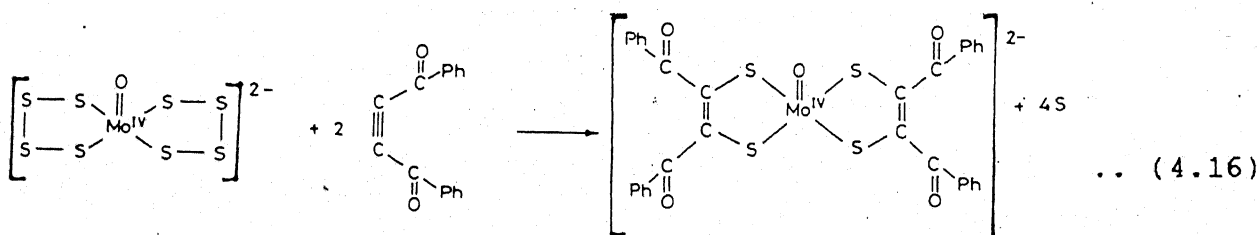
s = strong ; m = medium ; w = weak

Thus the bidentate coordination of $[\text{CS}_3]^{2-}$ group facilitates the electron transfer across $\{\text{Mo}=\text{S}\}$ bond. The two electrons generated by the two S^{2-} groups to form one $(\text{S}_2)^{2-}$ are transferred to Mo(VI) to make it Mo(IV) which can now stabilize the coordinated bidentate $[\text{CS}_3]^{2-}$. Then in the second step, the electrophilic attack by carbondisulfide on one of the two sulfur atoms of the disulfide ligand with subsequent rearrangement may result in the perthiocarbonate ligand. This is reminiscent of the insertion of CS_2 on the coordinated $(\text{S}_2)^{2-}$ ligand reported by Coucouvanis et al [73]. In the whole of the above process, the electron transfer from $\text{S} \rightarrow \text{Mo}$ is accompanied by no external oxidant sharing any electron. Hence during the entire course, the reaction mixture remains EPR silent with respect to the formation of any Mo(V) species.

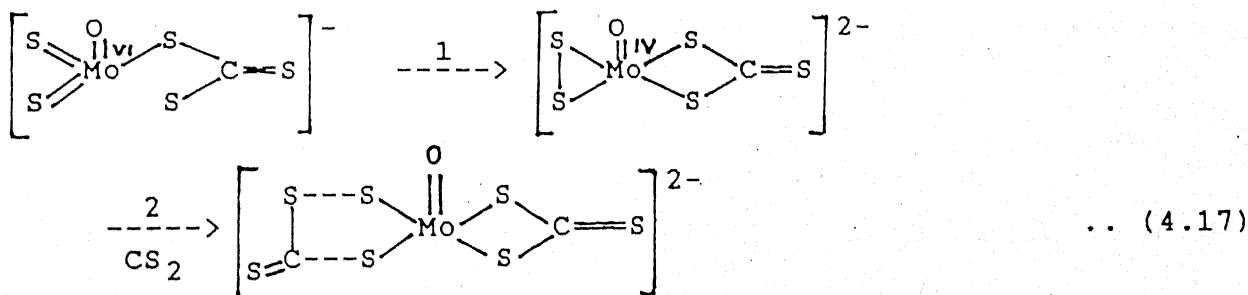
On the contrary when a protonated salt like $(\text{NH}_4)_2\text{MoS}_4$ is reacted with CS_2 in the presence of PPh_4Br , (Section 3.7.2) the compound isolated is $(\text{PPh}_4)_2[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_4]$. In this reaction apparently there is no formation of $(\text{S}_2)^{2-}$ as there is no perthiocarbonate ligand formed. Two important differences to be noted in this reaction compared to the previous one are (i) the use of protonated salt of $[\text{MoS}_4]^{2-}$, and (ii) the formation of an intermediate Mo(V) EPR active species (Fig 4.1.16). The balanced chemical reaction is as follows:



The reaction of $[\text{MoO}(\text{S}_4)_2]^{2-}$ with dibenzoyl acetylene (Section 3.6.2) results in the reduction of acetylene and the formation of bis(dithiolene) complex $[\text{MoO}(\text{S}_2\text{C}_2(\text{COPh})_2)_2]^{2-}$ as shown in equation 4.16. The insertion of acetylene does not take place across the {Mo-S} bond, instead it follows a cyclo addition process as found in the case of $[\text{MoS}(\text{S}_4)_2]^{2-}$ [31].

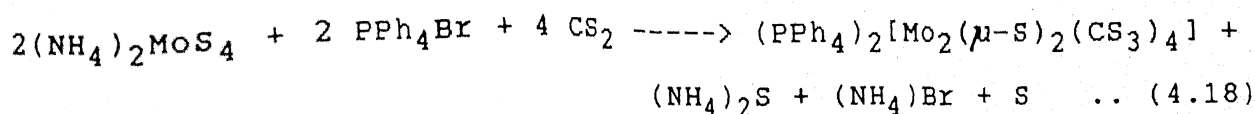


The formation of $(\text{PPh}_4)_2[\text{MoO}(\text{CS}_3)(\text{CS}_4)]$ (Section 3.7.1) by reacting $[\text{MoOS}_3]^{2-}$ with CS_2 in the absence of air is a very rare example of activation of electron transfer across {Mo=S} bond, activated by CS_2 . The formation of thiocarbonate ligand suggests a nucleophilic attack of one of the sulfido group on the carbon of CS_2 . The formation of $[\text{CS}_3]^{2-}$ in this reaction is very much similar to the hydroxyl mechanism for the activation of CO_2 in carbonic anhydrase [122]. The nucleophilic attack is followed by enhancement of the coordination number of Mo from 4 to 5 as shown in the first step of equation 4.17.

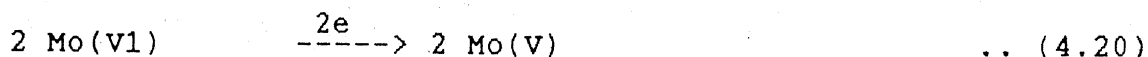
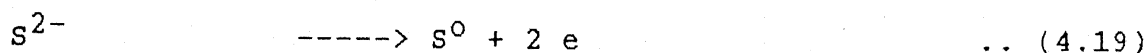


Thus the bidentate coordination of $[\text{CS}_3]^{2-}$ group facilitates the electron transfer across $\{\text{Mo}=\text{S}\}$ bond. The two electrons generated by the two S^{2-} groups to form one $(\text{S}_2)^{2-}$ are transferred to Mo(VI) to make it Mo(IV) which can now stabilize the coordinated bidentate $[\text{CS}_3]^{2-}$. Then in the second step, the electrophilic attack by carbondisulfide on one of the two sulfur atoms of the disulfide ligand with subsequent rearrangement may result in the perthiocarbonate ligand. This is reminiscent of the insertion of CS_2 on the coordinated $(\text{S}_2)^{2-}$ ligand reported by Coucouvanis et al [73]. In the whole of the above process, the electron transfer from $\text{S} \rightarrow \text{Mo}$ is accompanied by no external oxidant sharing any electron. Hence during the entire course, the reaction mixture remains EPR silent with respect to the formation of any Mo(V) species.

On the contrary when a protonated salt like $(\text{NH}_4)_2\text{MoS}_4$ is reacted with CS_2 in the presence of PPh_4Br , (Section 3.7.2) the compound isolated is $(\text{PPh}_4)_2[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_4]$. In this reaction apparently there is no formation of $(\text{S}_2)^{2-}$ as there is no perthiocarbonate ligand formed. Two important differences to be noted in this reaction compared to the previous one are (i) the use of protonated salt of $[\text{MoS}_4]^{2-}$, and (ii) the formation of an intermediate Mo(V) EPR active species (Fig 4.1.16). The balanced chemical reaction is as follows:



The formation of one S^0 from S^{2-} can account for the release of two electrons received by two of the Mo centers to produce $\{Mo_2(u-S)_2\}$ moiety as shown below.

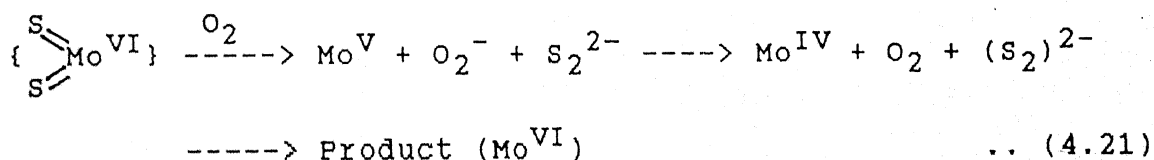


However this does not fit with the experimental observation of an EPR active Mo(V) species as a reactive intermediate suggesting the formation of a monomeric $\{Mo(V)\}$ moiety which ultimately dimerizes to yield the product. Furthermore stepwise release of electron from $S^{2-} \rightarrow S^- \rightarrow S^0$ is highly unlikely. As this reaction demands the use of protonated salt of $[MoS_4]^{2-}$ it is very likely that proton migration to one of the free sulfido groups occurs in the intermediate stages of the reaction where thiocarbonate groups are formed as described earlier (eq. 4.17). The ultimate formation of dimeric compounds is well established in pentavalent molybdenum chemistry where disulfido bridged compounds form to achieve the extra stability.

The involvement of external oxidant has been addressed in the next course of the reaction where $(Et_2NH_2)_2MoS_4$ has been treated with CS_2 under aerobic conditions (Section 3.7.3 Method B). The formation of EPR active species in the intermediate stage of the reaction and the demand for the protonated cationic salt is very similar as observed earlier. However, the role of

CS_2 in this reaction is dual in nature wherein it activates $\{\text{Mo}=\text{S}\}$ bond and also reacts with $(\text{Et}_2\text{NH}_2)^+$ moiety to produce dithiocarbamic acid (dtch). The dtc^- group functions as a bidentate ligand and the pentavalent dimeric neutral complex, $[\text{Mo}_2(\mu\text{-S})_2(\text{CS}_3)_2(\text{dtc})_2]$ is formed. Here, the role of aerial oxygen could be as an external oxidant to receive one electron out of the two released by the sulfido group. The other electron is used up in the reduction of Mo(VI) to Mo(V) . The dimerization takes place for the extra stability as seen in the earlier case.

When $[\text{MoOS}_3]^{2-}$ is used instead of $[\text{MoS}_4]^{2-}$ in the above reaction, the course of the reaction is totally different (Section 3.7.4 and 3.7.5). $[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNet}_2)_2]$ and a pentavalent dimeric complex, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNet}_2)_2]$ are isolated. The participation of Mo in the electron transfer process has been observed here also, in the form of EPR signal characteristic of Mo(V) . The formation of the hexavalent monomer as one of the final products can be viewed as a concealed induced electron transfer process which has already been established by us in the case of tungsten [56]. Thus the main electron-transfer pathway for the formation of the monomer can be described as shown in equation 4.21.



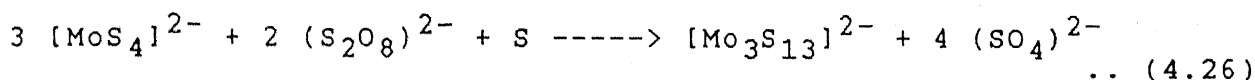
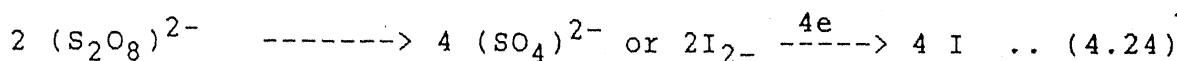
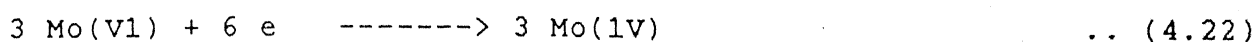
It has been observed that the tungsten analog $[\text{WO}(\text{S}_2)(\text{S}_2\text{CNET}_2)_2]$ undergoes dimerization with the formation of $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ either under thermal conditions or on keeping in solution for weeks [56]. In the case of molybdenum, the dimeric product, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNET}_2)_2]$ is isolated as one of the products within 2 hours. This is in accordance with the established observation that the rate of the reactions in molybdenum systems is much faster than in tungsten systems. The entire process of this ligand to metal electron flow is controlled by the external oxidant, oxygen, functioning as an electron acceptor. The role of Mo is to function as an electron sink which is similar to the role of molybdenum in the substrate reduction phase of Xanthine Oxidase turnover [123].

4.2.4 Reaction of $(\text{MoS}_4)^{2-}$ with I_2 or $(\text{S}_2\text{O}_8)^{2-}$

Recently it has been shown that elemental iodine can induce electron transfer across $\{\text{W}=\text{S}\}$ bond to yield $[\text{W}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ [21, 22]. As electron transfer across $\{\text{Mo}=\text{S}\}$ bond is more facile compared to $\{\text{W}=\text{S}\}$ bond, induction by iodine or even a better oxidizing agent like $(\text{S}_2\text{O}_8)^{2-}$ to provoke the surge of electrons can be envisaged. Thus when $(\text{Et}_2\text{NH}_2)_2\text{MoS}_4$ or $(\text{Et}_2\text{NH}_2)_2\text{MoOS}_3$ is reacted with I_2 , pentavalent dimeric molybdenum complexes are isolated according to Scheme 1. The formation of an EPR active monomeric intermediate has been verified by EPR spectroscopy.

From the present study, the role of polysulfide in the earlier reaction can be best described as that of an external oxidant. Apart from the role of external oxidants, the following similarity could be seen in both the reactions. In the polysulfide method, $[\text{Mo}_2\text{S}_{12}]^{2-}$ is formed as a by product whereas in the present study, $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ is isolated as a by-product. The formation of $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2)_2]^{2-}$ instead of $[\text{Mo}_2\text{S}_{12}]^{2-}$ may be due to the hydrolysis of the latter compound, which is proved by the formation of H_2S . However in all these reactions, the formation of Mo(IV) in low yield suggests that there may be more than one reaction pathway for such processes.

Interestingly when the rate of addition of I_2 is increased by hundred fold, in aqueous medium, $(NH_4)_2MoS_4$ in the presence of $(Et_4N)Br$ immediately precipitates $(Et_4N)_2[Mo_3S_9]$. The availability of $Mo(IV)$ so readily in aqueous medium under the influence of external oxidant directed us to look for a proper stoichiometric reaction where the external oxidant can induce electron transfer across $\{Mo=S\}$ bond to generate solely $Mo(IV)$ species. To achieve this, the following reaction scheme has been envisaged.



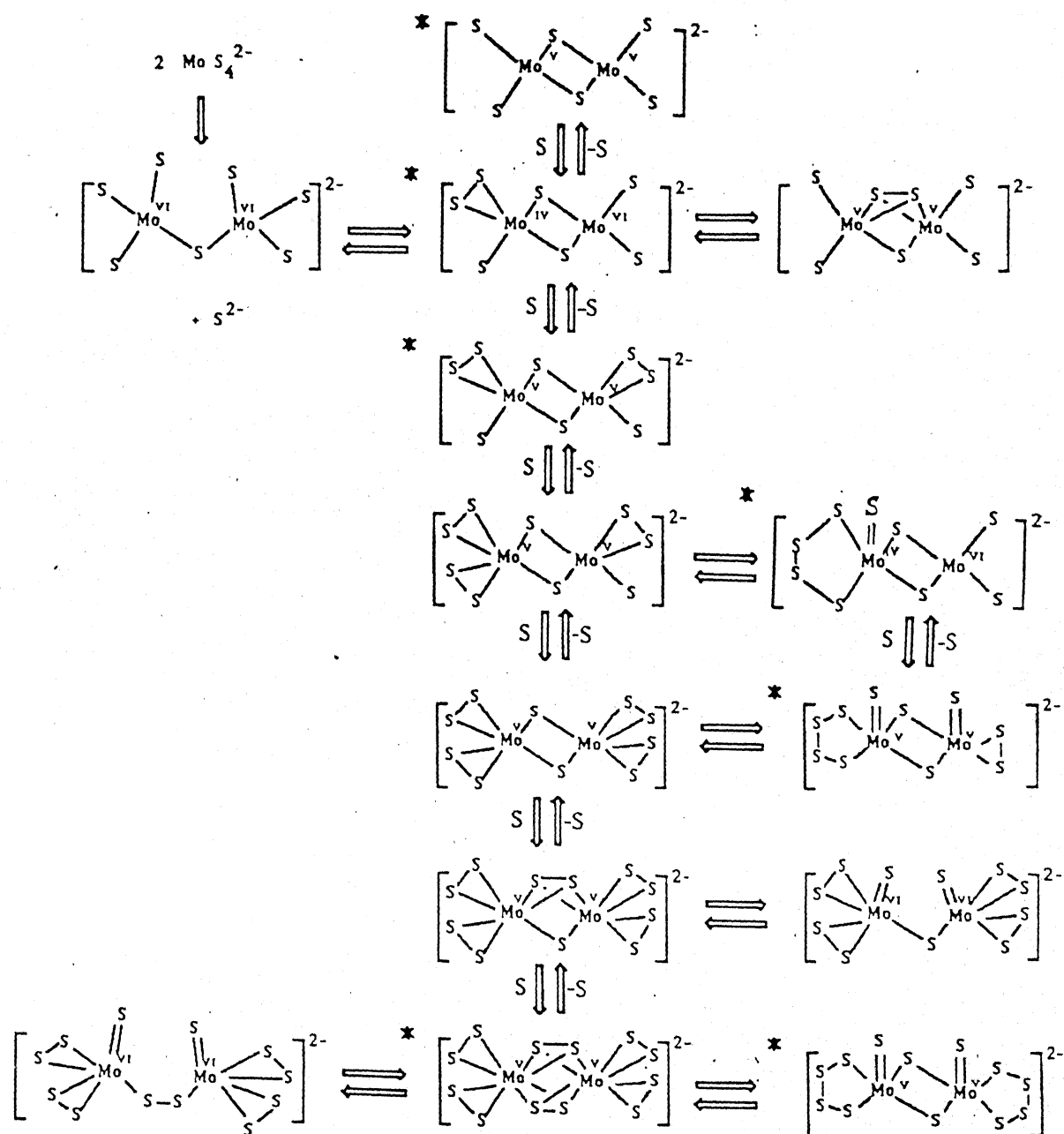
If it is possible to generate $Mo(IV)$ in aqueous medium, then according to equation 4.26, it should be possible to isolate the well known cluster complex $[Mo_3S_{13}]^{2-}$ under mild conditions. This tetravalent trinuclear cluster has been known to form by the treatment of polysulfide with $[MoS_4]^{2-}$ under high temperature [34, 36]. The same compound has been isolated at ambient conditions by using $(S_2O_8)^{2-}$ as external oxidant (vide section 3.8.3).

From the present study, the role of polysulfide in the earlier reaction can be best described as that of an external oxidant. Apart from the role of external oxidants, the following similarity could be seen in both the reactions. In the polysulfide method, $[\text{Mo}_2\text{S}_{12}]^{2-}$ is formed as a by product whereas in the present study, $[\text{Mo}_2\text{O}_2(\mu\text{-s})_2(\text{S}_2)_2]^{2-}$ is isolated as a by-product. The formation of $[\text{Mo}_2\text{O}_2(\mu\text{-s})_2(\text{S}_2)_2]^{2-}$ instead of $[\text{Mo}_2\text{S}_{12}]^{2-}$ may be due to the hydrolysis of the latter compound, which is proved by the formation of H_2S . However in all these reactions, the formation of Mo(IV) in low yield suggests that there may be more than one reaction pathway for such processes.

transfer relationships is very important. The variation of pH and changing of the functional groups attached to the $\{=\text{C}-\text{H}\}$ moiety are crucial in dictating the net electronic effect at the carbon center undergoing nucleophilic attack by the oxygen of $[\text{MoOS}_3]^{2-}$.

Another aspect that could be exploited is the redox condensation reactions of $[\text{MoS}_4]^{2-}$ / $[\text{MoOS}_3]^{2-}$ in the presence of phosphate. This may contribute towards understanding the interaction of thiomolybdate with ATP. For several polythiomolybdates it is seen that the central Mo is reduced and flanked by coordinated $[\text{MoS}_4]^{2-}$ group for e.g. in $[\text{Mo}_3\text{S}_9]^{2-}$. If one can replace the coordinated $[\text{MoS}_4]^{2-}$ groups by $(\text{PO}_4)^{3-}$ or $(\text{HPO}_4)^{2-}$, the redox chemistry of such species may yield interesting results. The extension of such reactions using ATP may throw light in understanding the energetics of these reactions with respect to proton / electron transfer and hydrolysis of ATP.

Besides these biorelated work one can direct the attention towards the synthesis of other sulfur rich polythiometallates. As pointed out in the introductory chapter, molybdenum has a high affinity for sulfur and the simple monomeric thiomolybdates $[\text{MoO}_n\text{S}_{4-n}]^{2-}$ ($n = 0, 1$) are the starting materials for the synthesis of a variety of binary molybdenum-sulfido compounds. The formation of these sulfur rich polythiomolybdates involve very complex reactions. The

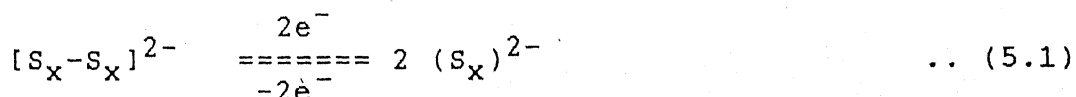


$[\text{Mo}_2(\text{S})_n(\text{S}_2)_{6-n}]^{2-}$ anions: plausible isomers and their interconversions. The starred entries have been characterized structurally. [Ref. 33]

FIG. 5.1

mechanism for the formation of many of these compounds has not been clearly understood and studies directed towards the mechanism of these reactions sounds a promising area of research for future work in this field. Coucouvanis and coworkers have proposed a reaction scheme for the equilibria between various Mo-S species as shown in Fig. 5.1 [33]. The salient features of this scheme are

- i) The proposal of a highly reactive intermediate $[\text{Mo}_2\text{S}_7]^{2-}$ with $\{\text{Mo(VI)}-\text{S}-\text{Mo(VI)}\}$ core which has relevance in the present study (vide Section 4.2.2).
- ii) The gain or loss of elemental sulfur or sulfide ligands.
- iii) The inclusion of internal electron transfer transfer in the structural transformation of some of these complex anions where oxidation or reduction of the molybdenum ions are effected by the breaking or making of S-S bonds. (eq. 5.1)



Some of the complexes shown in Fig. 5.1 have been isolated and structurally characterized. It is quite possible, that serendipitous, subtle changes in the synthetic procedures eventually may result in the stabilization and isolation of the other Mo-S complexes which may have interesting structural features.

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